U.S. DEPARTMENT OF COMMERCE
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PB-264 274

Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Volume VIII. Alumina/Aluminum Industry Report

Arthur D. Little, Inc, Cambridge, Mass.

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio

Dec 76

PB 264 274

EPA

Environmental Protection Agency
Office of Research and Development

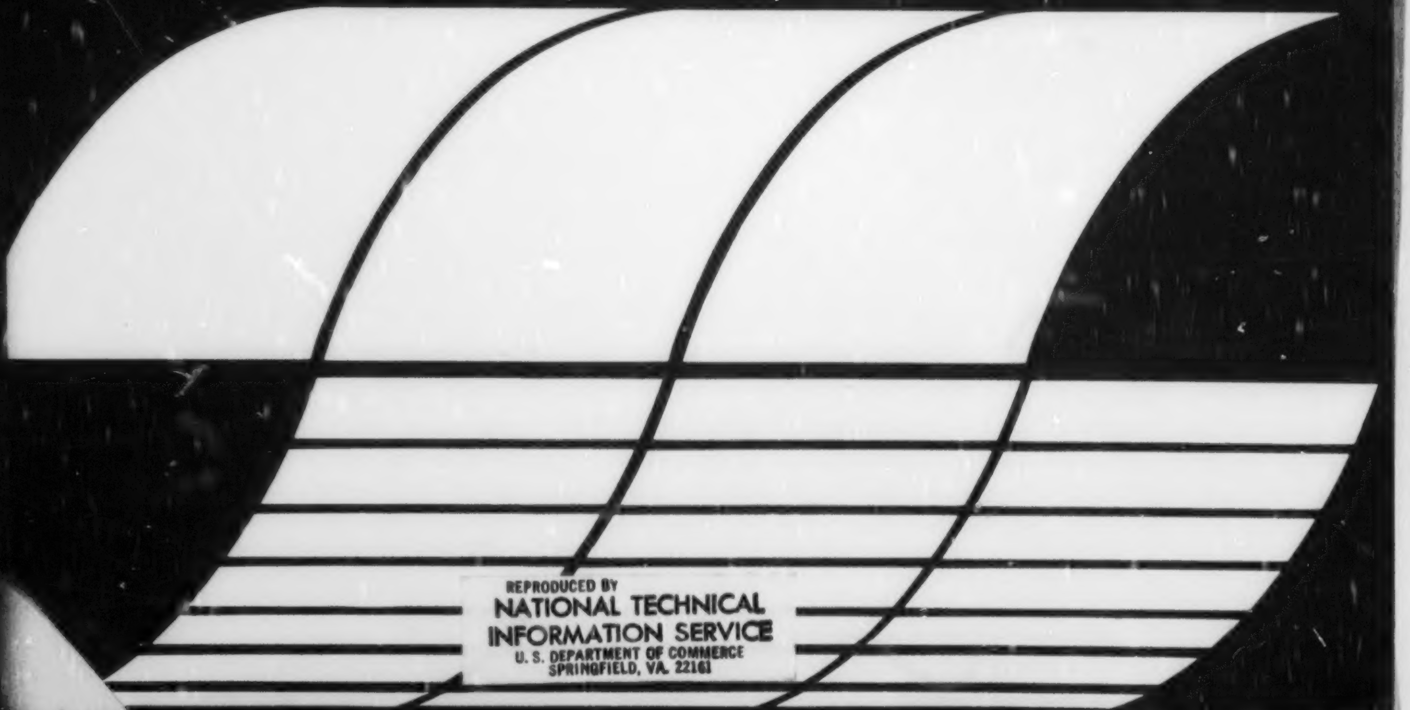
Industrial Environmental Research
Laboratory
Cincinnati, Ohio 45268

EPA-600/7-76-034h
December 1976

ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS:

Vol. VIII. Alumina/Aluminum Industry Report

Interagency
Energy-Environment
Research and Development
Program Report



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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-76-034h	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS Vol. VIII. Alumina/Aluminum Industry Report		5. REPORT DATE December 1976 issuing date 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. Acorn Park Cambridge, Massachusetts 02140		10. PROGRAM ELEMENT NO. EHE624B 11. CONTRACT/GRANT NO. 68-03-2198
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Enviornmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED FINAL 14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES Vol. III-VII, EPA-600/7-76-034c through EPA-600/7-76-034g, refer t studies of other industries as noted below; Vol. I, EPA-600/7-76-034a is the Industry Summary Report and Vol. II, EPA-600/7-76-034b is the Industry Priority Report.

16. ABSTRACT Report.

This study assesses the likelihood of new process technology and new practices being introduced by energy intensive industries and explores the environmental impacts of such changes. Specifically, Vol. VIII deals with the alumina/aluminum industry. The report examines three new process developments for producing alumina from domestic clays as alternatives to the Bayer process: (1) nitric acid leaching process, (2) hydrochloric acid leaching process, (3) clay chlorination (such as the Toth alumina process), and two process changes for the production of aluminum: (1) the Alcoa chloride electrolysis process and (2) the application of titanium diboride cathodes to the conventional Hall-Heroult cells. All of these alternatives are discussed in terms of relative process economics and environmental/energy consequences. Vol. III-VII and Vol. IX-XV deal with the following industries: iron and steel, petroleum refining, pulp and paper, olefins, ammonia, textiles, cement, glass, chlor-alkali, phosphorus and phosphoric acid, copper, and fertilizers. Vol. I presents the overall summation and identification of research needs and areas of highest overall priority. Vol. II, prepared early in the study, presents and describes the overview of the industries considered and presents the methodology used to select industries.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Energy Pollution Industrial Wastes Alumina Aluminum	Manufacturing Processes; Energy Conservation; Bayer, Hall Processes; Toth, Clays, Alcoa Process	13B

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 155
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/7-76-034h
December 1976

ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS

Volume VIII

ALUMINA/ALUMINUM INDUSTRY REPORT

EPA Contract No. 68-03-2198

Project Officer

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For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This study, consisting of 15 reports, identifies promising industrial processes and practices in 13 energy-intensive industries which, if implemented over the coming 10 to 15 years, could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives. The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary. Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction. The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

EXECUTIVE SUMMARY

The aluminum industry is comprised of two basic operations: (1) the production of alumina (Al_2O_3) from bauxite by the Bayer process, and (2) the reduction of alumina to aluminum metal by the Hall-Heroult electrolytic reduction process. These two operations are conducted at entirely separate locations.

Alternatives to the Bayer process examined in this study were hydrochloric acid leaching, nitric acid leaching, and high temperature chlorination (Toth process) of clays. The Alcoa chloride process and the use of titanium diboride cathodes were examined as potential future alternatives to the conventional Hall-Heroult process for aluminum production. In addition, the combination of clay chlorination and the Alcoa process was compared with the conventional Bayer-Hall technology.

Alumina

There are nine alumina plants within the U.S., six on the Gulf Coast, two in Arkansas, and one in the Virgin Islands with a total capacity of 7,700,000 short ton/yr. The only domestic source of bauxite, the major raw material in the production of alumina, is in Arkansas. The U.S. industry has always depended largely on imports from the Carribean, northern South America, and Australia for most of its supply of bauxite and alumina. Recent high levies on the bauxite exports and organized pressure to carry out the alumina production in these countries make it unlikely that new Bayer alumina plants will be built in the United States. However, if a successful clay-based process is developed, new alumina plants may be built in the United States based on domestic alumina-bearing kaolin and anorthosite clays, giving the United States some raw material independence.

It is clear that more solid waste will be produced from treating clays to recover alumina by any of the new processes--namely, nitric acid leaching, hydrochloric acid leaching or clay chlorination--than is produced by the existing Bayer alumina process. However, with the processing plant near the mines, the clay process wastes can be returned to mined-out areas.

In the case of the nitric acid and hydrochloric acid leaching processes, the tail gases from the decomposition-acid recovery operation could contain oxides of nitrogen and hydrogen chloride. Both could be removed by caustic scrubbing, but would result in water soluble nitrates and chlorides. The liquid waste from the nitric acid process will contain soluble nitrates. The hydrochloric acid and Toth chlorination processes will produce wastes containing soluble chlorides, which are generally less objectionable than soluble nitrates when discharged to the water environment.

Airborne emissions from the existing Bayer alumina plants are minor, limited largely to SO_2 emissions from the boiler house, depending on the fuel used, and dust from alumina and lime calcination. All can be controlled to meet existing regulations. Nevertheless, pollution control costs would be greater for any of the clay-based processes than those of the present Bayer process, but not prohibitively high considering the value of the product. In fact, the major environmental cost in nitric acid leaching is for sulfur dioxide control, since coal is used as a fuel source. In costing the hydrochloric acid leaching process low-sulfur fuel oil has been used as a fuel.

In comparing total energy use, the nitric acid leaching and clay chlorination processes appear to use about the same amount of energy, while hydrochloric acid leaching uses about 30% more energy per ton of alumina. In addition, hydrochloric acid leaching appears to entail the highest operating costs while nitric acid leaching costs compare favorably with those of a new Bayer plant. The lowest estimated operating costs are found in clay chlorination. Since energy use for clay chlorination is comparable to nitric acid leaching energy use, future work on clay chlorination bears watching to prove out the energy use and economics assumed here.

Aluminum

There are thirty-one aluminum smelters within the U.S., located along the Mississippi and Ohio Rivers; in Massena, New York; and in Washington, Oregon, and Western Montana. Total U.S. capacity is estimated at 5.0 million short ton/yr. World consumption of aluminum has historically experienced a long-term growth rate on the order of 10%/year. In the 1960's U.S. consumption grew by an average 8%/year, but the trend among U.S. producers has been to lose market share to foreign sources and to locate a larger amount of their smelter capacity outside the United States; 15% is now located abroad.

Until recently, there has been little incentive in the United States to reduce power consumption in aluminum smelters, which have traditionally been located in low-cost electric power areas, in many cases a considerable distance from their markets. Much of this power is hydroelectric; but with limited hydroelectric resources to be developed in the United States, this energy source is not expected to play a major role in the expansion of the U.S. aluminum industry.

The use of titanium diboride cathodes would not significantly change the nature of the liquid waste problem from the present operation. The new Alcoa chloride process would introduce a new source of liquid and solid waste arising as a consequence of bleeding the recirculating electrolyte. This waste would consist of oxide sludges and sodium chloride.

It seems likely that the Alcoa chloride process and the use of the titanium diboride cathodes in the existing Hall process will reduce air pollution from cells and from the anode-making and -baking operations. In the case of the Alcoa chloride process, the anodes will be inert and permanent, which means that air pollution from anode-making would be completely eliminated from the aluminum plant. In the case of the use of titanium diboride cathodes, the fluoride emissions per ton of aluminum produced would probably remain the same, but the gas volume to be scrubbed would be lower. Moreover, we would expect less carbon monoxide emissions per ton of aluminum produced.

Air pollution control costs for the cells and cell rooms of the new Alcoa process and for use of titanium diboride cathodes in Hall cells appear to be less than the costs for the existing Hall process. The Alcoa process would be completely enclosed in order to recover chlorine for reuse and, while there might be some losses of chlorine to the atmosphere, controlling chlorine emissions to required levels should not be as difficult as for fluoride emissions. However, the Alcoa process would add a new source of gaseous emissions, namely, sulfur from the coking step and hydrogen chloride from the chlorinator tail gas. Of course, both emissions can be controlled as required.

The Alcoa chloride process offers a potential route to making aluminum that has energy savings of about 10% while keeping operating costs the same or slightly lower than a plant based on Hall cell technology. The combination of a clay chlorination process with the Alcoa process shows significant potential cost savings. The estimated cost of complete environmental control of aluminum plants is a significant factor in both the capital and operating costs of aluminum smelters, amounting to about 9% of the investment and 4% of aluminum production costs in new Hall plants. We believe that the costs of achieving environmental standards should be reviewed and that the possibilities for improving the capital and operating costs of the pollution control system used in Hall cells should be investigated. We also suggest that materials research be undertaken on the subject of titanium diboride cathodes suitable in quality to permit long operating life in the Hall cell environment. This development would have a dramatic effect on energy savings in the aluminum industry. With minimal capital charge requirement, such a development can be retrofitted to existing aluminum plants. Other things remaining equal, there would be a favorable environmental effect in reducing the emissions from the power plants producing electricity for the smelters.

This report was submitted in partial fulfillment of contract 68-03-2198 by Arthur D. Little, Inc. under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 9, 1975 to December 1, 1975.

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ACKNOWLEDGMENTS

This study could not have been accomplished without the support of a great number of people in government agencies, industry, trade associations and universities. Although it would be impossible to mention each individual by name, we would like to take this opportunity to acknowledge the particular support of a few such people.

Dr. Herbert S. Skovronek, Project Officer, was a valuable resource to us throughout the study. He not only supplied us with information on work presently being done in other branches of EPA and other government agencies, but served as an indefatigable guide and critic as the study progressed. His advisors within EPA, FEA, DOC, and NBS also provided us with insights and perspectives valuable for the shaping of the study.

During the course of the study we also had occasion to contact many individuals within industry and trade associations. Where appropriate we have made reference to these contacts within the various reports. Frequently, however, because of the study's emphasis on future developments with comparative assessments of new technology, information given to us was of a confidential nature or was supplied to us with the understanding that it was not to be credited. Therefore, we extend a general thanks to all those whose comments were valuable to us for their interest in and contribution to this study.

Finally, because of the broad range of industries covered in this study, we are indebted to many people within Arthur D. Little, Inc. for their participation. Responsible for the guidance and completion of the overall study were Mr. Henry E. Haley, Project Manager; Dr. Charles L. Kusik, Technical Director; Mr. James I. Stevens, Environmental Coordinator; and Ms. Anne B. Littlefield, Administrative Coordinator.

Members of the environmental team were Dr. Indrakumar L. Jashnani, Mr. Edmund H. Dohnert and Dr. Richard Stephens (consultant).

Within the individual industry studies we would like to acknowledge the contributions of the following people.

Iron and Steel:	Dr. Michel R. Mounier, Principal Investigator Dr. Krishna Parameswaran
Petroleum Refining:	Mr. R. Peter Stickles, Principal Investigator Mr. Edward Interess Mr. Stephen A. Reber Dr. James Kittrell (consultant) Dr. Leigh Short (consultant)

Pulp and Paper:	Mr. Fred D. Iannazzi, Principal Investigator Mr. Donald B. Sparrow Mr. Edward Myskowski (consultant) Mr. Karl P. Fagans Mr. G. E. Wong
Olefins:	Mr. Stanley E. Dale, Principal Investigator Mr. R. Peter Stickles Mr. J. Kevin O'Neill Mr. George B. Hegeman
Ammonia:	Mr. John L. Sherff, Principal Investigator Ms. Nancy J. Cunningham Mr. Harry W. Lambe
Aluminum:	Mr. Richard W. Hyde, Principal Investigator Ms. Anne B. Littlefield Dr. Charles L. Kusik Mr. Edward L. Pepper Mr. Edwin L. Field Mr. John W. Rafferty
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Primary Copper:	Dr. Ravindra M. Nadkarni, Principal Investigator Dr. Michel R. Mounier Dr. Krishna Parameswaran
Fertilizers:	Mr. John L. Sherff, Principal Investigator Mr. Roger Shamel Dr. Indrakumar L. Jashnani

ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	Metre^2	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	Metre^3	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t^\circ_C = (t^\circ_F - 32)/1.8$
Degree Rankine	Degree Kelvin	$t^\circ_K = t^\circ_R/1.8$
Foot	Metre	0.3048
Foot^3/minute	Metre^3/sec	0.0004719
Foot^3	Metre^3	0.02831
Foot^2	Metre^2	0.09290
Foot/sec	Metre/sec	0.3048
Foot^2/hr	Metre^2/sec	0.00002580
Gallon (U.S. liquid)	Metre^3	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	Metre^3	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

I. INTRODUCTION

A. BACKGROUND

Industry in the United States purchases about 27 quads* annually, approximately 40% of total national energy usage.** This energy is used for chemical processing, raising steam, drying, space cooling and heating, process stream heating, and miscellaneous other purposes.

In many industrial sectors energy consumption can be reduced significantly by better "housekeeping" (i.e., shutting off standby furnaces, better thermostat control, elimination of steam and heat leaks, etc.) and greater emphasis on optimization of energy usage. In addition, however, industry can be expected to introduce new industrial practices or processes either to conserve energy or to take advantage of a more readily available or less costly fuel. Such changes in industrial practices may result in changes in air, water or solid waste discharges. The EPA is interested in identifying the pollution loads of such new energy-conserving industrial practices or processes and in determining where additional research, development, or demonstration is needed to characterize and control the effluent streams.

B. CRITERIA FOR INDUSTRY SELECTION

In the first phase of this study we identified industry sectors that have a potential for change, emphasizing those changes which have an environmental/energy impact.

Industries were eliminated from further consideration within this assignment if the only changes that could be envisioned were:

- energy conservation as a result of better policing or "housekeeping,"
- better waste heat utilization,
- fuel switching in steam raising, or
- power generation.

---

*1 quad = 10^{15} Btu

**Purchased electricity at an approximate fossil fuel equivalence of 10,500 Btu/kWh.

After discussions with the EPA Project Officer and his advisors, industry sectors were selected for further consideration and ranked using:

- Quantitative criteria based on the gross amount of energy (fossil fuel and electric) purchased by industry sector as found in U.S. Census figures and from information provided from industry sources. The aluminum industry purchased 0.59 quads out of the 12.14 quads purchased in 1971 by the 13 industries selected for study, or 2.2% of the 27 quads purchased by all industry (see Table I-1).
- Qualitative criteria relating to probability and potential for process change, and energy and effluent consequences of such changes.

In order to allow for as broad a coverage of technologies as possible, we then reviewed the ranking, eliminating some industries in which the process changes to be studied were similar to those in another industry planned for study. We believe the final ranking resulting from these considerations identifies those industry sectors which show the greatest possibility of energy conservation via process change. Further details on this selection process can be found in the Industry Priority Report prepared under this contract (Volume II).

On the basis of this ranking method, the aluminum industry, exclusive of the mining aspects, appeared in sixth place among the 13 industrial sectors listed.

C. CRITERIA FOR PROCESS SELECTION

In this study we have focused on identifying changes in the primary production processes which have clearly defined pollution consequences. In selecting those to be included in this study, we have considered the needs and limitations of the EPA as discussed more completely in the Industry Priority Report mentioned above. Specifically, energy conservation has been defined broadly to include, in addition to process changes, conservation of energy or energy form (gas, oil, coal) by a process or feedstock change. Natural gas has been considered as having the highest energy form value followed in descending order by oil, electric power, and coal. Thus, a switch from gas to electric power would be considered energy conservation because electric power could be generated from coal, existing in abundant reserves in the United States in comparison to natural gas. Moreover, pollution control methods resulting in energy conservation have been included within the scope of this study. Finally, emphasis has been placed on process changes with near-term rather than long-term potential within the 15-year span of time of this study.

In addition to excluding from consideration better waste heat utilization, "housekeeping," power generation, and fuel switching, as mentioned above, certain options have been excluded to avoid duplicating work being funded under other contracts and to focus this study more strictly on "process changes." Consequently, the following have also not been considered to be within the scope of work:

TABLE I-1

SUMMARY OF 1971 ENERGY PURCHASED IN SELECTED INDUSTRY SECTORS

	Industry Sector	10^{15} Btu/Yr.	SIC Code In Which Industry Found
1.	Blast furnaces and steel mills	3.49 (1)	3312
2.	Petroleum refining	2.96 (2)	2911
3.	Paper and allied products	1.59	26
4.	Olefins	0.984 (3)	2818
5.	Ammonia	0.63 (4)	287
6.	Aluminum	0.59	3334
7.	Textiles	0.54	22
8.	Cement	0.52	3241
9.	Glass	0.31	3211, 3221, 3229
10.	Alkalies and chlorine	0.24	2812
11.	Phosphorus and phosphoric acid production	0.12 (5)	2819
12.	Primary copper	0.081	3331
13.	Fertilizers (excluding ammonia)	0.078	287

(1) Estimate for 1967 reported by FEA Project Independence Blueprint, p. 6-2, USGPO, November 1974.

(2) Includes captive consumption of energy from process byproducts (FEA Project Independence Blueprint)

(3) Olefins only, includes energy of feedstocks: ADL estimates

(4) Ammonia feedstock energy included: ADL estimates

(5) ADL estimates

Source: 1972 Census of Manufactures, FEA Project Independence Blueprint, USGPO, November 1974, and ADL estimates.

- Carbon monoxide boilers (however, unique process vent streams yielding recoverable energy could be mentioned);
- Fuel substitution in fired process heaters;
- Mining and milling, agriculture, and animal husbandry;
- Substitution of scrap (such as aluminum, iron, glass, reclaimed textiles, and paper) for virgin materials;
- Production of synthetic fuels from coal (low- and high-Btu gas, synthetic crude, synthetic fuel oil, etc.); and
- All aspects of industry-related transportation (such as transportation of raw material).

D. SELECTION OF ALUMINA/ALUMINUM INDUSTRY PROCESS OPTIONS

Within each industry, the magnitude of energy use was an important criterion in judging where the most significant energy savings might be realized, since reduction in energy use reduces the amount of pollution generated in the energy production step. Guided by this consideration, candidate options for in-depth analysis were identified from the major energy consuming process steps with known or potential environmental problems.

After developing a list of candidate process options, we assessed subjectively

- pollution or environmental consequences of the process change,
- probability or potential for the change, and
- energy conservation consequences of the change.

Even though all of the candidate process options were large energy users, there was wide variation in energy use and estimated pollution loads between options at the top and bottom of the list. A modest process change in a major energy consuming process step could have more dramatic energy consequences than a more technically significant process change in a process step whose energy consumption is rather modest. For the lesser energy-using process steps process options were selected for in-depth analysis only if a high probability for process change and pollution consequences was perceived.

Because of the time and scope limitations for this study, we have not attempted to prepare a comprehensive list of process options or to consider all economic, technological, institutional, legal or other factors affecting implementation of these changes. Instead we have relied on our own background experience, industry contacts, and the guidance of the Project Officer and EPA advisors to choose promising process options (with an emphasis on near-term potential) for study.

In our view, process changes in the aluminum industry will be in response to the four major problems confronting the industry today:

1. dependence on foreign sources of raw material;
2. heavy energy requirement at a time of rising energy costs;
3. rising pollution control costs; and
4. almost prohibitively high construction costs for new conventional alumina and aluminum plants.

These problems will, in our view, lead to an emphasis on the following new approaches:

- In Raw Material Preparation

  1. There is growing industry interest in the possibilities of producing alumina from domestic alumina-bearing raw materials--alunite, kaolin, and anorthosite clays--and dawsonite, a sodium aluminum carbonate mineral found in oil shale. The latter is longer range since those who have investigated the possibility of dawsonite as a source of alumina from the industry have concluded that this source will only be economic if the shale is mined and retorted for its oil content, as a result of which the residue would be a byproduct source of alumina. It cannot be justified on the alumina content alone. However, clays are more easily mined by simple surface methods and therefore considered as a potential shorter term source of alumina for reduction to aluminum.

     Thus, with respect to alumina for aluminum production, we have considered in this study three new process developments for producing alumina from domestic clays as the alternative to the Bayer process, which is not suitable for treating clays:

     a) Nitric acid leaching process,

     b) Hydrochloric acid leaching process, and

     c) Clay chlorination such as the Toth alumina process.

     The first two are considered because the U.S. Bureau of Mines study of 23 identified processes and process variations for producing alumina from domestic clays showed them to be the most economic. We have also included clay chlorination, such as the Toth alumina process, because we believe that it has merit and might prove to be economical. Moreover, it might provide a source of raw material for the Alcoa chloride process which uses aluminum chloride as the feed to the cells.

2. We have not considered the improvement of the thermal efficiency of the Bayer process plants by increasing heat-transfer where surface fouling occurs due to scaling of heat-transfer surfaces. This can be improved by providing more heat exchangers to permit more frequent cleaning of surface ara and better heat-transfer coefficients. This does not qualify as a process change; moreover, the addition of more heat exchangers will be made when justified by higher fuel costs.

   We have not considered the installation of so-called fluid flash calciners developed by Alcoa for calcining the product alumina hydrate to alumina, and replacing the older, less efficient rotary kilns that have been used. We did not consider it because it is basically an equipment change and does not represent a really significant effect on the total energy consumption (the order of 1% of the total energy consumed to make aluminum from its basic raw materials).

- In Aluminum Smelting

  We considered the following as candidate process changes for the production of aluminum that relate strongly to the problem of energy conservation:

  1. The Alcoa chloride electrolysis process; and

  2. The application of titanium diboride cathodes to the existing Hall-Heroult cells.

  We have not considered other means of reducing the electrical consumption from the considered average of 15,600 kWh/short ton to the best known practice of about 12,000 kWh/ton in existing smelters. This is attainable largely as a result of reducing the anode current densities with an attendant reduction in the capacity of the cells which, of course, means replacing existing small cells with large cells and adding cell capacity, both of which would be very expensive. This is discussed in Appendix B, but is not further considered in this study, because it is not a process change but rather a change in equipment and operations.

Recognizing that capital investments and energy costs have escalated rapidly in the past few years and have greatly distorted the traditional basis for making cost comparison, we believe that the most meaningful economic assessment of new process technology can only be made by using 1975 cost data to the extent possible. Consequently, in estimating operating costs we have developed costs representative of the first half of 1975 using constant 1975 dollars for our comparative analysis of new and current processes.

II. FINDINGS AND CONCLUSIONS

A. PROCESS CHANGES IN PRODUCTION OF ALUMINA

1. Solid Waste

It is clear that more solid waste will be produced from treating clays to recover alumina by any of the new processes - namely, nitric acid, hydrochloric acid leaching, or clay chlorination - than is produced by the existing Bayer alumina process. Since bauxite used in the Bayer process contains about 50% alumina, while clay contains typically only 30-35% alumina, there is simply more inert material. However, with the processing plant near the clay mines, the waste can be returned to mined-out areas. In the case of a Bayer alumina plant, the bauxite is imported and space must be found to dispose of the solid waste ("red mud") from the process.

2. Liquid Waste

With respect to liquid waste, in the case of the nitric acid process the liquid wastes will contain soluble nitrates, whereas with the hydrochloric acid and clay chlorination processes, the wastes will contain soluble chlorides which are generally less objectionable than soluble nitrates when discharged to the water environment. If complete impoundment in an impervious barrier-lined disposal area is required ("zero discharge"), the pollution control costs would be greater for any of the clay-based processes than for the present Bayer alumina plants.

3. Gaseous Emissions

The gaseous emissions from the existing Bayer alumina plants are minor, limited largely to gaseous emissions from the boiler house, which would be SO_2, depending on the fuel used and the dust from alumina and lime calcination, both of which can be controlled to meet existing regulations.

In the case of the nitric acid and hydrochloric acid leaching processes, the tail gases from the decomposition-acid recovery operation could contain oxides of nitrogen and hydrogen chloride, both of which could be removed by caustic scrubbing, but this would result in water-soluble nitrates and chlorides.

It would appear that more effective control, e.g., zero discharge, might be necessary in the case of nitrates from the nitric acid process than might be required for chlorides from the hydrochloric acid or clay chlorination processes and for the solid and liquid wastes from the present Bayer alumina process.

Table II-1 qualitatively compares the air, water and solid waste streams from the various process options considered.

TABLE II-1

AIR, WATER, AND SOLID WASTE STREAMS FROM BASE CASE AND PROCESS MODIFICATIONS

Process Alternative Alumina	Air Emission	Water Effluent Streams	Solid Waste
Bayer (base case)	• Dust from alumina grinding • Calciner flue gas	• Thickener underflow	Red mud
Hydrochloric acid leaching	• Dust from alumina grinding • HCl-containing tail gas from acid recovery plant	• Thickener underflow • Scrubber water from HCl scrubbing waters (caustic)	Waste clay
Nitric acid leaching	• Calciner flue gas (SO_2 + particulates) • Nitrogen oxide-containing tail gas from acid recovery plant	• Thickener underflow • Scrubber waters (caustic)	Waste clay
Clay chlorination (Toth)	• Calciner flue gas (SO_2 and particulates) • Tail gas exhaust from chlorinator • Flushing of chlorinator purge material	• Cooling tower blowdown	Waste clay

4. Costs and Energy Use

Table II-2 shows energy use and the cost of pollution control for production of alumina. In the Bayer process both energy use and costs are small, considering the present value of alumina at $125/ton and the projected cost of more than $200.00/ton in new Bayer plants. The cost for complete environmental control of the new clay-based leaching processes is estimated to be higher, but not prohibitively high, considering the value of the product. The major environmental cost in HNO_3 leaching involves SO_2 control, since coal is used as a fuel source, while natural gas or low-sulfur fuel oil is the basis used for costing the HCl leaching process based on information available to us in early 1976.*

From a cost and energy viewpoint, the clay alumina process appears very attractive. Thus future work on this process to verify the energy use and economics assumed here bears watching.

B. CHANGES IN PRODUCTION OF ALUMINUM

1. Air Pollution

It seems likely that the Alcoa process and the use of titanium diboride cathodes will reduce air pollution from the cells and from the anode-making and -baking operations. In the case of the Alcoa chloride process, the anodes will be inert, which means that anodes would be purchased rather than produced at the plant. Thus, air pollution from anode-making in the Alcoa process would be completely eliminated from the aluminum plant. When titanium diboride cathodes are used, the fluoride emissions per ton of aluminum produced would remain the same, but the gas volume to be scrubbed would be lower. Moreover, we would expect less carbon monoxide emissions per ton of aluminum produced.

It would appear that costs for air pollution control from the cells and cell rooms of the new Alcoa process and for the use of titanium diboride cathodes in the Hall process would be less than the costs for the existing process. The Alcoa process would be completely covered to recover chlorine for reuse and, while there might be some losses of chlorine to the atmosphere, controlling chlorine emissions to required levels should not be as difficult as for fluoride emissions.

However, the Alcoa process would add a new source of gaseous emissions, namely, sulfur from the coking step and hydrogen chloride from the chlorinator tail gas. Of course, both can be removed as required.

2. Liquid and Solid Waste

The use of titanium diborides would not significantly change the nature of the liquid waste problem from the present operations. The new Alcoa process

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*If natural gas at $1.85/10^6$Btu in the HCl leaching process could be replaced 100% by coal at $0.82/10^6$Btu, it would 1) decrease energy costs by about $39/ton alumina, 2) increase pollution control costs by about $25-30, and 3) result in a net reduction of about $9-14/ton alumina.

TABLE II-2

SUMMARY OF RESULTS OF PROCESS OPTIONS IN THE ALUMINA INDUSTRY

(Basis: 700,000 annual tons alumina production)

	Units	Base Line Bayer Process (New)	Hydrochloric Acid Leaching	Nitric Acid Leaching	Clay Chlorination (Toth)
Production Facility					
Capital investment	$\$10^6$	280	430	322	232.6
Production cost*	\$/ton	235.37	320.72	226.28	179.29
Energy requirements	10^6 Btu/ton	14.53	39.21	26.76	28.59
Environmental Control Facilities					
Fixed capital investment	$\$10^6$	0.89	0.28	14.03	8.55
Operating cost*	\$/ton	1.40	5.00	19.00	0.80
Energy requirements	10^6 Btu/ton	0.056	0.016	0.695	0.293
Production plus Environmental Control Facilities					
Fixed capital investment	$\$10^6$	280.89	430.28	336.03	241.15
Total cost* of production	\$/ton	236.77	325.72	245.28	190.09
Energy requirements	10^6 Btu/ton	14.59	39.23	27.46	28.88

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* Includes pretax return on investment

would introduce a new source of liquid and solid waste arising as a consequence of bleeding off impurities from the electrolyte. This would consist of sludge and sodium chloride.

3. Costs and Energy Use

The estimated cost of complete environmental control of aluminum plants is a significant factor in both the capital and operating costs of aluminum smelters. It amounts to about 9% of the investment and 3.7% of aluminum production costs in new Hall plants, as shown in Table II-3.

Alcoa chloride process offers a potential route to making aluminum that has energy savings of about 10%, while keeping operating costs the same or slightly lower than for a plant based on Hall cell technology. Pollution control costs are significantly lower because of the elimination of fluoride emissions. Table II-4 shows that the combination of clay chlorination with the Alcoa process results in significant cost savings. However, we recognize that additional research is required to prove out the economics of such a concept. Energy use is comparable to the base line Bayer-Hall process combination.

4. Practices or Processes Requiring Additional Research

We believe that the EPA should review requirements for the Hall process and look into possibilities for improving the capital and operating costs of the pollution control systems used. We also suggest that the U.S. Government consider the possibility of undertaking or sponsoring materials research in the field of titanium diboride cathodes suitable in quality to permit long operating life in the Hall-Heroult cell environment. This development would have a dramatic effect on energy savings in the aluminum industry. With minimal capital charge requirement, such a development can be retrofitted to existing aluminum plants. With lower power consumption and other things remaining equal, there would be favorable environmental effects per ton of aluminum produced in reducing the CO emissions from aluminum cells and emissions from power plants.

TABLE II-3

SUMMARY OF RESULTS OF PROCESS OPTIONS IN THE ALUMINUM INDUSTRY BASED ON BAUXITE

(Basis: 160,000 annual tons aluminium)

		Existing Facility		New Plant	
	Units	Hall	Hall with TiB_2	Hall (Baseline)	Alcoa Chloride
Production Facility					
Capital investment	$\$10^6$	140[a]	182[b]	280	280
Production cost*	\$/ton aluminum	698	696	1,137	1,107
Energy requirements	10^6 Btu/ton	187.82	151.18	150.02	135.10
Environmental Control Facilities					
Fixed capital investment	$\$10^6$	28.48	29.90	28.48	4.23
Operating cost*	\$/ton aluminum	44	37.2	44	16.5
Energy requirements	10^6 Btu/ton	1.71	1.31	1.71	0.42
Production plus Environmental Control Facilities					
Fixed capital investment	$\$10^6$	168.48	169.90	308.48	284.23
Total cost* of production	\$/ton aluminum	742	733	1,181	1,123
Energy requirements	10^6 Btu/ton	189.53	152.49	151.73	135.52

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*Includes pretax return on investment

(a) Estimated undepreciated investment

(b) Estimated undepreciated investment with TiB_2 modification to produce 208,000 annual tons aluminum

TABLE II-4

SUMMARY OF RESULTS OF PROCESS OPTIONS OF COMBINED PROCESSES IN PRODUCTION OF ALUMINUM

(Basis: 160,000 annual tons aluminum)

	Units	Base Line Bayer Alumina plus Hall (New)	Alternative Process Clay Chlorination - Alcoa
Production Facility			
Capital investment	$\$10^6$	403	296
Production cost*	\$/ton	1,372.37	1,032
Energy requirements	10^6 Btu/ton	164.55	160.24
Environmental Control Facilities			
Fixed capital investment	$\$10^6$	29	12
Operating cost*	\$/ton	46.72	37.35
Energy requirements	10^6 Btu/ton	1.77	0.99
Production plus Environmental Control Facilities			
Fixed capital investment	$\$10^6$	432	308
Total cost* of production	\$/ton	1,419	1,069
Energy requirements	10^6 Btu/ton	166.32	161.23

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*Includes pretax return on investment

III. INDUSTRY OVERVIEW

This chapter presents a general description of the aluminum industry; further detail is provided in Appendix A.

The aluminum industry is comprised of two basic operations:

(1) the production of alumina from bauxite by the Bayer process, and

(2) the reduction of alumina to aluminum metal by the Hall-Heroult electrolytic reduction process.

These two operations are conducted at entirely separate locations.

There are nine alumina plants within the United States. Six are located on the Gulf Coast, because of requirements for receiving imported bauxite and the availability of natural gas as a low cost fuel; two are in Arkansas, originally for proximity to local bauxite deposits, which were the only major domestic sources of bauxite in the United States; and one is in St. Croix, the Virgin Islands. With the exception of the St. Croix facility, these plants are all relatively old, the oldest having begun operation in 1940 and the rest in the late '40's and early '50's. Individual plant capacities range from 1.385 million to 370,000 short ton/yr with the total U.S. capacity equal to 7.7 million short ton/yr. By modern standards these plants are small. Most new installations being built abroad have a capacity of at least 1 million and more typically 2 million short ton/yr.

The only domestic source of bauxite, the major raw material in the production of alumina, is the Arkansas bauxite deposits. The U.S. industry has always depended largely on imports for most of its supply of bauxite and alumina, and as the quality of Arkansas bauxite has become poorer, this dependency on foreign sources has increased. Primary sources of U.S. bauxite imports are the Caribbean, northern South America, and Australia. Recent activity on the part of source countries in the form of high levies on the bauxite exported and organized pressure to carry out the alumina production in these countries have placed substantial strain of the U.S. aluminum industry. For these reasons it is unlikely that new Bayer alumina plants will be built in the United States. However, if a successful process based on an alternative raw material is developed, such as a domestic clay-based process (as discussed in Chapter IV), we could see new alumina plants being built in the United States. They would be based on domestic alumina-bearing raw materials, principally the kaolin and anorthosite clays, the use of which would promote some raw material independence.

There are 31 aluminum smelters within the United States. These are owned by 12 aluminum companies, six of which also produce alumina domestically. These aluminum plants are located in three general areas:

- along the Mississippi and Ohio Rivers due to the availability of low-cost coal as fuel and the transportation system provided by the rivers;
- in Massena, New York, because of the St. Lawrence River transportation system and low-cost hydroelectric power; and
- in Washington, Oregon, and western Montana, also because of low-cost hydroelectric power.

Half of the existing smelters have been in operation for 20 years. These are both Soderberg and prebake smelters. Within the last 15 years, all smelters that have been constructed have been prebake, because Soderberg smelters require 2-10% more power. Total U.S. capacity is estimated at 5.019 million short ton/yr; with individual plant capacities ranging from 285,000 short ton/yr to 36,000 short ton/yr. Alcoa, Kaiser, and Reynolds are the largest producers with Alcoa controlling 1.580 million ton/yr, Kaiser 724,000 ton/yr, and Reynolds 975,000 ton/yr.

Through 1973 world consumption of aluminum experienced a long-term growth rate on the order of 10% per year. U.S. consumption has risen gradually over the years with the exception of a period during the 1940's when wartime need for aircraft production caused a sharp rise in the curve. The building and construction industries are the largest end-users of aluminum (22% of the market in 1974), with transportation (18%), packaging (17%), electrical users (14%), and consumer durable goods (9%) also playing major roles. Of these, packaging and transportation are the fastest growing markets.

In the 1960's U.S. consumption grew by an average [illegible]% per year (compared to rates of 4-5% per year for steel and copper). Between 1960 and 1970, the United States' dominant position in terms of smelter capacity began to erode, falling from 53% of the world total to 45%. The trend among U.S. producers to locate a larger amount of their smelter capacity outside the United States continues; 15% is now located abroad.

The financial condition of the aluminum industry is a matter of growing concern. The rapid rate of growth of the industry has generated heavy capital requirements; the industry's requirement of $1.50-2.00 of capital investment per $1.00 of annual sales is about three times the average for all industry. Since a major share of the industry's capital is borrowed, the cost of money has had a severe impact on aluminum costs.

Until recently there has been no incentive in the United States to reduce power consumption. Aluminum smelters have traditionally been located in low-cost electric power areas - in many cases a considerable distance from their markets. Much of this power is hydroelectric, but with limited hydroelectric resources to be developed in the United States, hydroelectric power is not expected to play a major role in the expansion of the United States aluminum industry. Thus, with no really cheap power left, freight costs, capital and interest charges, and tariffs have become important site-selection factors.

Although the basic Hall-Heroult process for the reduction of alumina to aluminum has not really changed since its introduction over 70 years ago, important design and engineering changes have evolved. During the past 40-50 years commercial cells have increased in size more than threefold and have diminished 35-40% in power consumption. Modern cell lines are more mechanized and labor requirements in the cell rooms have been reduced to a minimum. In the 1960's, costs were reduced about 10%, largely by reducing power consumption through the use of larger cells with larger anodes, but it is likely that further cost reduction in the 1970's will be limited.

The aluminum industry has grown rapidly by making metal available when it was needed and at a price which made it economically attractive to users. If supply is allowed to drop below demand for an appreciable period, list prices will increase and some of the incentive to use aluminum would be lost. On the other hand, the present downturn in demand has caused prices to weaken, despite significant production cutbacks.

The industry is presently concerned that as the cost of power increases, the cost and price of aluminum will increase and aluminum may lose some of its share of the metals market to alternative materials. This is the reason for the present research and development activity in the industry that has as its objective reducing energy consumption, particularly in the smelting of alumina to aluminum, where nearly all of the energy required to produce aluminum is consumed.

In addition, there is growing interest in producing alumina from domestic alumina-bearing raw materials, principally clays, to reduce the dependence on imported raw materials. Their cost has been increasing, as mentioned earlier, in spite of the fact that energy consumption is likely to be higher for producing alumina from clays than for producing alumina from imported bauxite.

IV. COMPARISON OF CURRENT AND ALTERNATIVE PROCESSES

The production of aluminum is and will continue to be a two-step operation consisting of:

1. Refining of alumina-bearing raw materials (bauxite or clays) to high-purity alumina or possibly aluminum chloride; and

2. Conversion of high-purity alumina or aluminum chloride to molten aluminum by high-temperature molten salt electrolysis.

In the recent past (1950's to early 1960's), there was much research and development work done on the so-called "direct reduction" of alumina-bearing raw materials to aluminum. Several alternative methods were considered, but none showed any real promise and thus all have been abandoned. Based on these very disappointing experiences, it is extremely unlikely that this activity will be renewed.

A. ALUMINA PRODUCTION

1. Status

With respect to alternative process options for the first step in aluminum production, i.e., the production of alumina, all present efforts in the United States and other industrial countries are being directed toward recovering alumina from alternative domestic alumina-bearing raw materials, largely clays. The U.S. aluminum industry is based almost entirely on imported raw materials in the form of bauxite or alumina. The threat of the formation of an international bauxite cartel by the bauxite-producing countries and the drastically increased cost of these raw materials have made U.S. aluminum companies particularly interested in domestic clays as an alternative raw material. Kaolin and anorthosite clays are available in abundance and at low cost in the United States; in fact, a much lower cost, based on an alumina content, than imported bauxite. No activity is currently being extended to developing an alternative to the Bayer process for refining high-grade imported bauxite to alumina, nor is there an incentive to do so. However, for a variety of reasons, there is particular interest in production of alumina from the large reserves of kaolin clay in Georgia and South Carolina.

Renewed interest in the technology and economics of producing alumina from domestic raw materials has led the U.S. Bureau of Mines to undertake a program to investigate the more promising clay-based processes in their laboratory at Boulder City, Nevada. The Bureau recently estimated capital and operating costs for a number of processes proposed for producing alumina from kaolin and anorthosite clays. Based on the Bureau of Mines' Information Circular 8648, published in 1975, the following processes appear to have the lowest operating costs and therefore to be the most attractive: (1) the hydrochloric acid leaching-liquid, ion exchange process, and (2) the nitric acid leaching-liquid ion exchange process (developed by Arthur D. Little, Inc).

Interest continues in many of these leaching processes, in spite of the prospect of higher energy consumption and higher capital costs than are required for the construction and operation of Bayer alumina plants operated on imported bauxite. In addition, the Toth alumina process, which involves production of alumina and byproduct crude titanium dioxide by chlorination of clay in the presence of carbon, appears to have potential merit and low costs, although this process would have higher energy requirements than the Bayer process (29×10^6 Btu for Toth vs 15×10^6 Btu for Bayer).

Accordingly, we have evaluated these alternative process options for the production of alumina in terms of cost, energy requirements, and effluents produced. To achieve a meaningful evaluation, we have compared these processes with the process presently being used to produce alumina in the United States (the Bayer process). We have included the more prominent of the clay-based processes, despite the fact that energy consumption is higher than that of the Bayer alumina process for the following reasons:

(1) The aluminum industry is interested in these processes as a means of limiting future escalation in prices of imported alumina or bauxite;

(2) The U.S. Government is concerned with an increasing balance-of-payments problem; and

(3) These processes have environmental implications.

2. Current U.S. Alumina Technology (Bayer Process)

At present, the sole technology used to produce alumina in the United States is the Bayer process, which is discussed in detail in Appendix B. This process is old and well developed, having first been introduced in 1888, but it is applicable only to bauxite as the raw material. This process has the ability to treat both trihydrate and monohydrate bauxites, although the cost for treating monohydrate bauxite, used in European Bayer plants, is much higher. Most of the Bayer plants located in the United States are old and largely depreciated. These plants operate on the more easily treated trihydrate bauxites imported from the Caribbean. Tables IV-1 and IV-2 show estimated costs for both an existing plant and a new plant, based on the Bayer process. Highlights of these tables are summarized below.

a. Costs

The average cost of alumina from an existing U.S. Bayer alumina plant is estimated to be about \$125/short ton of Al_2O_3. Capital costs for new Bayer alumina capacity, as of March 1975, was about \$400/ton of annual alumina capacity. The nominal minimum economic size of a Bayer plant would be about 700,000 short ton/yr of alumina. Capital investment for this size installation would be \$280 million. Present costs for alumina, including return on investment, produced from a new Bayer installation, would be \$237/short ton.

TABLE IV-1

ESTIMATED PRODUCTION COSTS IN "EXISTING" BAYER ALUMINA PLANTS, 1975

Product: Alumina

Process: Bayer

Location: Texas

Annual Capacity: 700,000 net tons

Capital Investment: (CI)*

Annual Production: 700,000 net tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
• Bauxite	Net ton	23.00	2.40	55.20
• Limestone	Net ton	5.00	0.133	0.67
• Soda Ash	Net ton	68.00	0.075	5.10
Energy				
• Natural Gas	10^6 Btu	0.70	11.64	8.15
• Electric Power Purchased	kWh	0.014	275.00	3.85
• Misc.				
Water				
• Process	10^3 gal	0.50	2.00	1.00
• Cooling	10^3 gas	0.05	2.75	0.14
Direct Operating Labor (Wages)	Man-hr	6.50	0.88	5.72
Direct Supervisory Wages	15% Op. Lbr			0.86
Maintenance Labor (Wages)	Man-hr	6.50	0.80	5.20
Maintenance Supervision (Wages)	15% Mnt. Lbr			0.78
Maintenance Materials & Supplies	1.5% of RC			6.00
Labor Overhead	32% of wages			4.02
Misc. Variable Costs/Credits				
• Starch	Net ton	180.00	0.006	1.08
TOTAL VARIABLE COSTS				97.77
FIXED COSTS				
Plant Overhead	60% of wages			7.54
Local Taxes and Insurance	2% of RC			8.00
TOTAL PRODUCTION COSTS				113.31
Capital Charges	5% of UI			10.00
Pollution Control				1.40
TOTAL				124.71

*Undepreciated Capital Investment (UI) $140,000,000
Replacement Cost (RC) $280,000,000

TABLE IV-2

ESTIMATED PRODUCTION COSTS IN "NEW" BAYER ALUMINA PLANTS, 1975

Product: Alumina　Process: Bayer　Location: Texas

Annual Capacity: 700,000 net tons　Capital Investment: (CI) $280,000,000　Annual Production: 700,000 net tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
● Bauxite	Net ton	23.00	2.40	55.20
● Limestone	Net ton	5.00	0.133	0.67
● Soda Ash	Net ton	68.00	0.075	5.10
Energy				
● Purchased Fuel[a]				
- Fuel Oil or Gas	10^6 Btu	1.85	11.64	21.53
● Electric Power Purchased	kWh	0.015	275.00	4.13
● Misc.				
Water				
● Process	10^3 gal	0.50	2.00	1.00
● Cooling	10^3 gas	0.05	2.75	0.14
Direct Operating Labor (Wages)	Man-hr	6.50	0.88	5.72
Direct Supervisory Wages	15% Op. Lbr.			0.86
Maintenance Labor (Wages)	Man-hr	6.50	0.80	5.20
Maintenance Supervision (Wages)	15% Mnt. Lbr.			0.78
Maintenance Materials & Supplies	1.5% of CI			6.00
Labor Overhead	32% of wages			4.02
Misc. Variable Costs/Credits				
● Starch	Net ton	180.00	0.006	1.08
TOTAL VARIABLE COSTS				111.43
FIXED COSTS				
Plant Overhead	60% of wages			7.54
Local Taxes and Insurance	2% of CI			8.00
Depreciation	7.1% of CI			28.40
TOTAL PRODUCTION COSTS				155.37
Return on Investment (pretax)	20% of CI			80.00
Pollution Control				1.40
TOTAL				236.77

(a)e.g., misc. chemicals, catalysts, supplies, services.

b. Energy Consumption

The average energy consumption in Bayer alumina plants in the United States is rather moderate, amounting to 275 kWh and 11.64×10^6 Btu/ton of alumina. On a fossil fuel basis (10,500 Btu/kWh), this amounts to 14.53×10^6 Btu/ton of alumina.

c. Effluent Control

Details of effluent control for the Bayer alumina plants are discussed in Appendix C with investments and operating costs summarized in Tables IV-3 and IV-4, respectively. Details are discussed below:

(1) Water and Solid Waste

The first operation in the Bayer plant is the unloading of imported bauxite, a partially dried bulk material consisting of both lump and fines. Unloading is effected by normal grab bucket means, which is a possible but minor point of air pollution, i.e., the dust is typically uncontrolled. The bauxite carriers are primarily dedicated to the bauxite trade with minor backhaul opportunity limited to backhauling caustic or coal to the source, caustic for Bayer plant operation at the source, and coal as fuel for the foreign Bayer plant operations. In either case, there is no need to clean the holds before loading either coal or caustic solution.

The principal waste streams from the Bayer alumina plants are a red mud stream, spent liquor purges, steam condensate, barometric condenser and other indirect cooling water systems, and storm water run-off. Of these, the red mud solid waste in slurry form is by far the most important, because it is the major stream in terms of both solid and liquid wastes. The cost of achieving zero discharge is largely the cost of red mud pond construction, piping, and neutralization, and of other equipment necessary for proper operation of the recycle system. The estimated water pollution control cost ranges from about \$0.30 to \$0.60/ton of alumina, as detailed in Appendix C (Table C-3). For our calculations here we use a figure of \$0.48/ton of alumina, shown in Table IV-3 as amounting to \$336,000 for producing 700,000 tons of alumina per year.

(2) Air

Emissions to the atmosphere consist entirely of dust from the following operations: grinding bauxite and calcining alumina and limestone. The latter may or may not be carried out at the alumina plant. Emissions from these sources are rather easily controlled at the source with air cleaning equipment at an insignificant or relatively small cost.

(3) Energy

Energy requirements for pollution are shown to be about 0.06×10^6 Btu/ton of alumina, as shown in Table IV-5, which is small compared to the 14.5×10^6 Btu/ton of alumina used on the process side.

TABLE IV-3

CAPITAL INVESTMENT SUMMARY FOR ENVIRONMENTAL CONTROL* IN ALUMINA INDUSTRY

(Basis: 700,000 ton/yr alumina production)

	Baseline	Alternative Process		
	Bayer	HCl	HNO_3	Toth
Air Pollution Control Investments ($000)				
Dust from alumina or clay grinding	85	175	--	--
Flue gas from calciner				
• particulates	800	--	1,700	1,331
• SO_2	--	--	12,200	6,588
HCl from acid recovery	--	100	--	276
NO_x from acid recovery	--	--	125	--
Total	885	275	14,025	8,195
Other pollution control costs	--	--	--	355**
TOTAL	885	275	14,025	8,550

Source: Arthur D. Little, Inc., estimates

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*Process solids and wastewaters are discharged to a pond and are calculated as an annual operating cost, instead of as a capital investment (see Table IV-4 and discussion in text).

**Treatment of cooling tower blowdown (see Table IV-8).

TABLE IV-4

ANNUAL OPERATING COST SUMMARY FOR ENVIRONMENTAL CONTROL IN ALUMINA INDUSTRY

(Basis: 700,000 ton/yr alumina production)

	Baseline	Alternative Process		
	Bayer	HCl	HNO_3	Toth
Water and/or Solid Pollution Control Costs* ($000)				
Ponding of process solids & wastewaters	336	3,260	1,810	1,444
Cooling tower blowdown				155
Total	336	3,260	1,810	1,599
Air Pollution Control Costs* ($000)				
Dust from alumina or clay grinding	52	110	--	--
Flue gas from calciner				
• particulates	600	--	1,180	925
• SO_2	--	--	10,200	4,790
HCl from acid recovery	--	85	--	231
NO_x from acid recovery	--	--	100	--
Total	652	195	11,480	5,946
Unit cost, $/ton alumina	$1.40	$5.00	$19.00	$10.80

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*Includes 20% return on capital invested (see text)

TABLE IV-5

ENERGY CONSUMPTION SUMMARY FOR ENVIRONMENTAL CONTROL IN ALUMINA INDUSTRY

(Basis: 700,000 ton/yr alumina production)

	Base Line	Alternative Process		
	Bayer	HCl	HNO_3	Toth
Water Pollution Control				
Electric power, 10^6 kWh/yr	0.052	0.23	0.13	0.048
Air Pollution Control				
Electric power, 10^6 kWh/yr	3.7	0.822	46.2	19.5
Total Electric Power, 10^6 kWh/yr	3.752	1.052	46.33	19.55
Total Fuel Equivalent*, 10^6 Btu/yr	39,396	11,046	486,500	205,275
Unit Energy Consumption, 10^6 Btu/ton alumina	0.056	0.016	0.695	0.293

Source: Arthur D. Little, Inc. estimates

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*@10,500 Btu/kWh

3. Alternative Alumina Production Processes

a. Hydrochloric Acid Ion Exchange Process

Briefly, in the hydrochloric acid ion exchange process, clay is dehydrated, leached with hydrochloric acid, and then settled to separate the residue from the aluminum chloride/iron chloride solution. This solution is then purified with an amine ion exchange system operation to remove the iron chloride, while leaving the aluminum chloride in solution. The aluminum chloride in the solution is crystallized from the solution and decomposed to alpha alumina, and the acid value is recovered. Details are described below and can be found in Figure IV-1.

(1) Leaching

Crushed, dehydrated clay is fed to leaching tanks operated at approximately 225°F where the clay is leached with 20% hydrochloric acid for about 1 hour. During leaching, 87% of the alumina in the dehydrated clay reacts to form aluminum chloride by the reaction:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

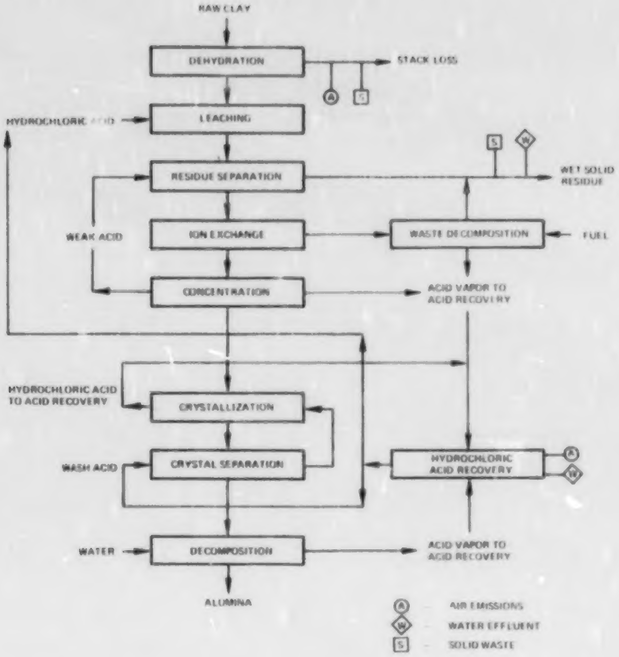
RAW CLAY
DEHYDRATION
STACK LOSS
A
S
HYDROCHLORIC ACID
LEACHING
S
W
RESIDUE SEPARATION
WET SOLID RESIDUE
WEAK ACID
ION EXCHANGE
WASTE DECOMPOSITION
FUEL
CONCENTRATION
ACID VAPOR TO ACID RECOVERY
HYDROCHLORIC ACID TO ACID RECOVERY
CRYSTALLIZATION
WASH ACID
CRYSTAL SEPARATION
HYDROCHLORIC ACID RECOVERY
A
W
WATER
DECOMPOSITION
ACID VAPOR TO ACID RECOVERY
ALUMINA
A - AIR EMISSIONS
W - WATER EFFLUENT
S - SOLID WASTE

Figure IV-1. Hydrochloric Acid-Ion Exchange Process

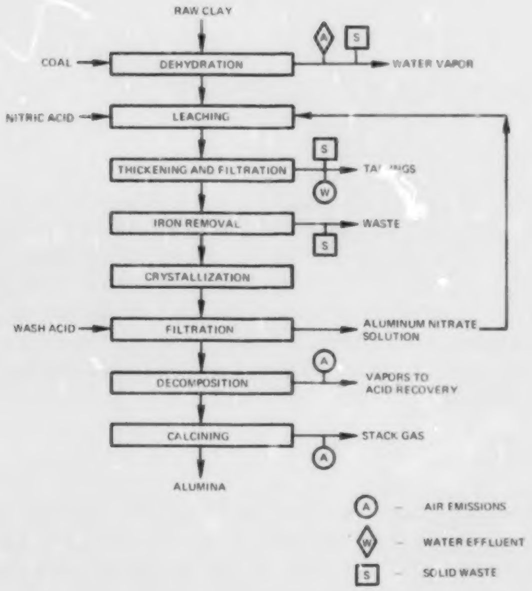
RAW CLAY
A
S
COAL
DEHYDRATION
WATER VAPOR
NITRIC ACID
LEACHING
S
THICKENING AND FILTRATION
TAILINGS
W
IRON REMOVAL
WASTE
S
CRYSTALLIZATION
WASH ACID
FILTRATION
ALUMINUM NITRATE SOLUTION
A
DECOMPOSITION
VAPORS TO ACID RECOVERY
CALCINING
STACK GAS
A
ALUMINA
A - AIR EMISSIONS
W - WATER EFFLUENT
S - SOLID WASTE

Figure IV-2. Nitric Acid-Ion Exchange Process

Also, according to the USBM, this solution contains about 85% of the iron present in the dehydrated clay in the form of ferric chloride. The leaching requires about 1% excess hydrochloric acid over that required for the various reactions involved in the leaching.

After leaching, the slurry is pumped to covered thickeners where the residue is separated from the solution. The solution is pumped to a surge tank and the residues washed with weak hydrochloric acid in a four-stage countercurrent washing thickener operation. Residue underflow from the washing circuit contains about 50% solids which are pumped to filters, reslurried with recycle waste water, and then pumped to a waste pond; finally, the overflow from the washing circuit is pumped to the surge tank.

(2) Ion Exchange

Ferric chloride contained in the solution must be removed to prevent contamination of the product. The solution from the surge tank in the leaching section is pumped to a three-stage countercurrent liquid ion exchange operation. Each stage is a mixer settler. The aluminum-iron containing solution is pumped to the mixer at one end of the circuit, and contacted with an amine kerosene alcohol liquid ion exchange mixture containing 4.7 volume % secondary amine, 10% n-decyl alcohol, and 85.3% by volume crude kerosene. This water-immiscible liquid is pumped to the mixer at the other end of the circuit. The contact is approximately 1 volume of ion exchange mixture per volume of iron-containing solution. All of the ferric chloride is transferred to the ion exchange mixture with essentially no loss of hydrochloric acid or aluminum chloride. The iron-free aluminum chloride solution is pumped to a surge tank in the crystallization and decomposition section and the iron-containing ion exchange mixture is pumped to a three-stage countercurrent regeneration system in which each stage is also a mixer-settler. About one ton of water per ton of ferric chloride is used to strip the ferric chloride from the ion exchange mixture. During the ion exchange regeneration operations, approximately 0.2 gallon of ion exchange mixture per 1000 gallons of feed solution is assumed to be lost to the purified aluminum chloride solution and the aqueous ferric chloride strip solution. Ion exchange mixture and makeup are recycled to the ion exchange circuit for reuse. The ferric chloride removed during regeneration is pumped to the waste decomposition section. The ultimate disposition of the lost ion exchange medium is discussed below.

(3) Crystallization and Decomposition

Iron-free aluminum chloride solution is pumped from the surge tank to the evaporators where the solution is concentrated. The vapor containing a small quantity of hydrochloric acid is condensed and recycled to the residue washing circuit in the leaching section. Concentrated solution from the evaporators is pumped from a surge tank where it is mixed with mother liquor recovered from aluminum chloride crystal separation. The solution is then pumped from the surge tank to crystallizers where aluminum chloride in the solution is crystallized as aluminum chloride hexahydrate by driving off water and hydrogen chloride. Vapor from the crystallizers is condensed and then pumped to the acid recovery section. The aluminum chloride hexahydrate is pumped from the crystallizers as a 35% solids slurry to continuous centrifuges where the crystals are separated from the mother liquor and are washed with 34% hydrochloric acid. Mother liquor and washings flow to a sump from which most of the solution is recycled to the surge tank feeding the crystallizers. To prevent a buildup of impurities and the crystallization of some impurities that would contaminate the product, part of the solution from the sump (1-2%, depending on the level of contaminants in the feed) is pumped to the waste solids decomposition section.

Aluminum chloride hexahydrate crystals recovered in the centrifuges are conveyed to fluidized bed reactors operated at 2000°F where the crystals are decomposed to alpha alumina, hydrogen chloride, and water vapor as shown in the reaction:

$$2(AlCl_3 \cdot 6H_2O) \rightarrow \alpha\ Al_2O_3 + 6HCl + 9H_2O.$$

The alpha alumina is cooled and conveyed to silos where it is stored until shipped, and vapors from the kiln are fed into the acid recovery section.

(4) Waste Solids Decomposition

Mother liquor purged from the crystallization and decomposition sections is fed directly to a crystallizer where acid vapor is driven off. This results in the crystallization of most of the aluminum chloride and impurities in the solution. Crystals are removed from the crystallizer and are fed to rotary kilns operating at 2000°F where the crystals are decomposed to yield acid which is sent to the acid recovery section. Acid vapors from the crystallizer are also condensed and sent to the acid recovery section.

A ferric chloride solution obtained from the regenerative operation in the ion exchange section is pumped to a fluid bed roaster operating at 1800°F where the ferric chloride reacts with water vapor to form ferric oxide and hydrogen chloride, according to the reaction:

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl.$$

Vapor from the spray roaster is sent to the acid recovery section, while the ferric oxide is cooled, mixed with recycle water from the waste pond and waste solids from the waste decomposition kiln, and pumped to the waste pond. This discarded solid waste material will contain undecomposable soluble chlorides such as chlorides of the alkali and alkali earth metals that can originate from the ore.

The small amount of organic amines, alcohols, and kerosene ion exchange medium that is lost to primary purified aluminum chloride product solution, or the stripped ferric chloride solution, would be largely steam-stripped during evaporation, ending up in the condensate from the evaporators. In the case of both the aluminum chloride solution and the stripping liquor, these materials would end up in condensed dilute hydrochloric acid, which goes to the residue washing end of the leaching circuit, thus to solids disposal. In addition, some of the 0.2 gallon of ion exchange liquid lost per 1000 gallons of feed solution would be lost because of the polymerization in the mixer settlers from which it has to be occasionally removed and incinerated or dumped.

(5) Acid Recovery

Acid vapors from the crystallization and decomposition sections and from the waste decomposition section are mixed with products of combustion from which the acid must be removed. The acid streams are combined and fed to the top of a cooler absorber, as is the 10% hydrochloric acid recycled from the tailings tower. Approximately 34% hydrochloric acid is produced in the cooler absorber and pumped to a surge tank. Lean gas from the cooler absorber is fed to the bottom of the packed tailings tower where practically all of the hydrogen chloride in the gas stream is absorbed by water to form a 10% hydrochloric acid solution. This 10% acid is pumped to the cooler absorber, while the exhaust gas from the packed tailings tower is vented to the atmosphere. This stream would require a caustic scrubbing system to remove any unabsorbed hydrogen chloride vapors with the scrubber discharge added to the residues discharged to the waste ponds.

Part of the hydrochloric acid produced in the cooler absorber is mixed with a small quantity of water and is then recycled to the aluminum chloride crystal washing operation in the crystallization and decomposition section. The rest of the hydrochloric acid is mixed with acid condensate (obtained from the crystallizers in the crystallization and decomposition section) and the waste decomposition section water and makeup acid to form 20% hydrochloric acid which is recycled to the leaching step.

(6) Status of the Process

The Anaconda Company operated a large-scale, pilot-plant operation using hydrochloric acid leaching at Butte, Montana during the late 1950's and early 1960's. The firm produced moderate quantities of pot feed alumina that was actually converted to aluminum in its aluminum smelter at Twin Butte, Montana.

In 1975 the U.S. Bureau of Mines tested this process, among others, at its laboratory at Boulder City, Nevada. The test work, partly supported by the aluminum industries, was carried out in a so-called mini-plant; i.e., a small integrated pilot plant. The results of this work have not yet been published.

No commercial plant embodying this process has ever been built and operated.

(7) Effluent Control

Water Pollution

The primary waste material from this process is the underflow from the series of thickeners, which consists of the acid-insoluble clay fraction and a dilute aluminum chloride aqueous solution which has a solids concentration of approximately 50%.

Based on information from the U.S. Bureau of Mines, an anticipated composition for this sludge stream (for the 700,000-ton/yr base case plant) is as follows:

Constituent	Quantity (ton/day)
Al_2O_3	1,720
S_iO_2	4,500
$AlCl_3$ (soluble)	91
Other soluble chlorides, Cl^-	200
Water	6,580
Other impurities	360
Total	13,451

This discharge is large, amounting to 6.7 ton/ton of alumina, nearly 50% of which is water. The major kaolin clay reserves are in the states of Georgia (primarily), South Carolina, and Alabama. In these states the rainfall exceeds the evapo-transpiration so that either water used for slurry transportation of the residues to the disposal pond would have to be eliminated, or recycle water from the disposal lagoons would have to be used. Ideally, recycle water from the disposal area should be used insofar as possible as process water makeup to the plant. However, the extent to which this could be accomplished is limited because of a soluble impurities buildup, as discussed below.

In addition to the major components - alumina, silica and iron oxides - the Georgia kaolin contains small amounts of calcium, magnesium, and titanium, plus a small amount of vanadium as oxide, sodium, potassium, manganese, phosphorous, zinc, lead, and tiny amounts of sulfur as sulfate, largely as calcium or magnesium sulfates. Considering the above, one would expect that soluble chlorides of calcium, sodium, potassium, zinc and lead might build up in any recycle loop. A small amount of phosphoric acid would also be present. Manganese would follow the iron and would be present in the solid tailings as manganese oxides, as would be the case with the iron discharged. Thus, it is doubtful that a completely closed-loop system would be possible. However, it is entirely possible that a closed-loop water recycle system could be used for transporting the solid residue to the disposal ponds by slurry.

The pollutants of major concern are the soluble chlorides, which include a number of the metals present in the clay. Because these wastes are acidic and the liquid effluents have a high total dissolved solid content, it is assumed that land disposal must be effected in an area where adequate provisions have been made to prevent percolation into groundwater and run-off into surface water. The most probable methods for disposal are either returning the leached clays to the pits, or placing them in specially designed aboveground impoundments. Although local geological conditions might permit returning them to the pits, it has been assumed that an above-ground, diked impoundment lined with an impervious liner, such as an elastomer membrane, would be used instead. Because the location of these alumina plants will be in geographical areas where the net rainfall exceeds the net evaporation, it will be necessary to institute a careful water management program with the process operation through recycle of water collected in the disposal logoons. When a disposal lagoon is filled, it is expected that a ground cover would be implaced to prevent leaching and lateral transport of water from rainfall. This procedure would create a disposal cell in a form which should require the least long-term management and with the high probability that all events, short of catastrophic happenings, would not cause the materials to enter the water environment.

It is estimated that the annual production of solid waste could be contained in an area 2050 x 2050 x 25 ft deep. The containing dikes would have inner and outer walls sloping at 45-deg angles and a 40-ft wide roadway on the top. It is estimated that the construction costs for such an impoundment would be $3,260,000 as shown in Table IV-4, which is equivalent to $4.66/ton of alumina. Because of the more elaborate construction envisioned as necessary for impoundments holding these chloride wastes than is necessary for Bayer process red-muds, the estimated solid waste disposal costs are significantly greater than the $0.48/ton of alumina from the Bayer process.

Air Pollution

This process is based upon the leaching of clays, such as kaolin, which generate as much dust as bauxite during grinding and initial calcination. The process does generate several waste gas streams containing HCl. These are sent to an acid recovery system where the HCl is stripped. However, tail gas from the acid recovery plant may contain small amounts of HCl. We assume that controls are necessary, which would require a caustic/spray tower scrubbing system, which should prove adequate, and the liquid discharge would go to the tailings ponds.

Pollution Control Costs and Energy

As shown in Table IV-4, pollution control costs for the HCl leaching alternative are estimated to be $5/ton of alumina compared to $1.40/ton for the Bayer process. Table IV-5 shows pollution control energy requirements are small and amount to only 0.016 x 10^6 Btu/ton of alumina.

(8) Process Energy Use

This process consumes 134 kWh of power plus 37.8 x 10^6 Btu of fossil fuel energy per ton of alumina, excluding the energy in the raw materials. Converted to a fossil fuel basis, i.e., including the inefficiencies in power generation (10,500 Btu/kWh), the total energy consumption amounts to 39.21 x 10^6 Btu/ton of alumina, which is considerably higher than the Bayer process in which the total energy consumption on a fossil fuel basis is only 14.53 x 10^6 Btu/ton of alumina.

(9) Capital and Operating Costs

We have reworked the Bureau of Mines' estimate on capital costs by updating these costs from the 1973 basis to an early 1975 basis, i.e., approximately March 1975. A 700,000-ton/yr alumina plant, based on the above-described hydrochloric acid leaching process, would cost $430 million, i.e., $615/annual ton of capacity. This compares with a standard or conventional Bayer plant cost (as of March 1975) of $400/annual ton of capacity. The estimated operating cost per ton of alumina, including return on investment, is shown in Table IV-6 to be $326/ton of alumina via the HCl leaching process. This compares unfavorably with existing Bayer alumina plants that can presently produce alumina at $125/ton, and even new Bayer plants that can produce alumina under present conditions at a cost of about $237/ton.

We have discussed the pollution control problems with the USBM personnel presently involved actively in pilot plant work on this process and other clay-based alumina processes. Their considered view is that all air streams containing particulate or gaseous emissions should be treated, and all resulting solid and liquid effluents should be discharged to a disposal area lined with an impervious barrier with subsequent ground cover implacement, as discussed and estimated above.

b. Nitric Acid Ion Exchange Process

Briefly, the nitric acid ion exchange process involves the following steps (see Figure IV-2):

1. Calcining the kaolin clay to make the contained alumina selectively available for extraction with nitric acid;
2. Leaching the calcined clay with hot nitric acid at atmospheric pressure to produce a solution of aluminum nitrate and a suspension of the clay-insolubles;
3. Separating the clay-insolubles from the aluminum nitrate liquor in thickeners;
4. Removing the iron and other impurities from the clarified aluminum nitrate liquor by use of a liquid ion-exchange medium;

TABLE IV-6

ESTIMATED PRODUCTION COSTS FOR NEW ALUMINA PLANT, 1975
(Hydrochloric Acid Leaching Process)

Product: Alumina

Process: Hydrochloric Acid Leaching

Location: Georgia

Annual Capacity: 700,000 tons

Capital Investment: (CI) $430,000,000

Annual Production: 700,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
• Clay (Kaolin)	ton	2.50	5.02	12.55
• Hydrochloric Acid	ton	27.00	0.14	3.78
Energy				
• Purchased Fuel				
- Natural Gas	10^6 Btu	1.85	37.80	69.93
• Electric Power Purchased	kWh	0.015	134.00	2.01
• Misc.				
Water				
• Process	10^3 gal	0.50	1.5	0.75
• Cooling	10^3 gal	0.05	64.00	3.20
Direct Operating Labor (Wages)	Man-hr	6.50	0.80	5.20
Direct Supervisory Wages	15% Op. Lbr.			0.78
Maintenance Labor (Wages)	Man-hr	6.75	1.55	10.08
Maintenance Supervision (Wages)	15% Mnt. Lbr.			1.51
Maintenance Materials	2% of CI			12.29
Labor Overhead	32% of wages			5.62
Misc. Variable Costs/Credits				
• Organic Solvent	lb.	0.30	4.39	1.32
• Operating Supplies				2.40
TOTAL VARIABLE COSTS				131.42
FIXED COSTS				
Plant Overhead	60% of wages			10.54
Local Taxes and Insurance	2% of CI			12.29
Depreciation	7.1% of CI			43.61
TOTAL PRODUCTION COSTS				197.86
Return on Investment (pretax)	20% of CI			122.86
Pollution Control				5.00
TOTAL				325.72

5. Removing the remaining impurities from the iron-free aluminum nitrate liquor by means of vacuum crystallization of aluminum nitrate nonohydrate;

6. Recovering the alumina by hydrolysis of the aluminum nitrate under controlled conditions so that the nitrate values are recovered largely as nitric acid rather than as nitrogen oxides;

7. Recovering the nitric acid and nitrogen oxide values in the form of nitric acid for recycle; and

8. Calcining the product alumina.

A more detailed discussion of the process, presented below, is based on extensive non-integrated pilot plant work, engineering experiments, and corrosion tests.

(1) Clay Preparation

The raw material input to the process consists of the clay produced by the mining and beneficiation of kaolin clay. Beneficiation consists of scrubbing the crude clay with water under agitation to thoroughly separate and disperse the kaolin particles into the water leaving behind a sand fraction. In this operation a hydroseparation takes place, and the kaolin is cleaned and recovered by thickeners and filtration. The clarified water is recycled. The washed clay is then extruded, dried, and fed to the calcination section of the process. The sand, if high grade, is valuable; but if not, it can be discharged to a designated site as a solid.

(2) Clay Calcination

The dried clay pellets are fed from a storage bin to a rotary kiln which is equipped with attached planetary tube coolers. The burning zone of the kiln is operated at 1475°F. The temperature of the discharged calcined clay from the cooler is expected to be 190°F. Kaolin clay, when heated to 1475°F for approximately one hour, loses its water of crystallization and the remaining alumino-silicate structure undergoes a transformation which reorders the aluminum and its associated oxygen atoms from their original regular sites in the lattice to an amorphous alumina and a skeleton of crystalline silica. Thus, more complete extraction of alumina is possible. Process steam is produced from the 800°F off-gas. Coal is used as direct-fired fuel for this step in the process. If high-sulfur coal is used, SO_2 scrubbing would be required. Part of the ash from coal firing would drop out in the calcined clay, but some fly ash would leave the kiln to be recovered from the off-gases along with the fine particulate from the clay. This material could be discharged dry to a designated disposal area or to residue disposal lagoons.

(3) Digestion

The calcined kaolin clay is charged to feed bins equipped with weight feeders which discharge into agitated leaching reactors. These reactors are constructed of titanium and operate at atmospheric pressure. They are vented through a reflux condenser in which the nitric acid vapors leaving the boiling solution in the reactor are condensed and totally refluxed to the reactor. However, the vents are manifolded to a vent line that goes to nitric acid recovery to take care of any gases emitted during the filling and charging operations.

The reaction which occurs between nitric acid and the alumina contained in the calcined clay is exothermic. That heat is extracted from the leaching reactors by letting the solution boil at atmospheric pressure and then condensing the vapors with return of the condensate. Therefore, the total heat of reaction leaves the system in the cooling water from the condenser.

Digested slurry is pumped from the bottom of each reactor. Nitric acid of sufficient concentration is metered directly from storage to each of the reactors. The leaching system is batch, which is favored over continuous in light of the important relationship between leach liquor composition and leaching time.

(4) Separation and Thickening

The digested slurry is pumped to the continuous countercurrent separation and thickening section. The thickeners would be 216 ft in diameter, concrete lined with fiber glass cloth-reinforced, polyester-interior coatings. This is based on a corrosion-materials of construction study.

An aqueous nitrate solution at any temperature above its crystallization point contains a sufficiently high concentration of nitric acid to make it corrosive, so that the heat exchangers interposed between the digestors and the first thickener to cool the slurry from 280°F to 160°F must be made of titanium to permit the use of the reinforced polyester in the first thickener. The high temperatures of the leach slurry sent to the first thickener would require a high cost lining since the first thickener will operate at a temperature close to the feed solution temperature (160°F).

The underflow from each thickener is mixed thoroughly with the overflow from the succeeding stages in agitated repulp tanks. The clarified overflow of aqueous aluminum nitrate solution product from the first thickener is fed through a surge tank to polishing filters before going to the purification section.

The waste material from the underflow of the last stage thickener, which consists of the acid insoluble clay fraction and a very dilute aluminum nitrate aqueous solution, is filtered and the filter cake repulped with recycle water and pumped to a lined storage lagoon.

(5) Purification

Iron and other impurities are extracted from the aluminum nitrate solution in three countercurrently operated mixer-settler liquid ion exchange extraction stages. The extractant is a di-2-ethylhexyl phosphoric acid (DEHPA) and tributyl phosphate (TBP) solution in kerosene. The extractors are agitated stainless-steel tanks. The settlers are made of the same material.

The aqueous phase from the settler enters a surge tank and then proceeds to the primary crystallizer where pure aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, is produced, while the other cation impurities are rejected. The crystals are separated from the mother liquor by centrifugation and sent on to the hydrolysis step. The mother liquor is sent to a secondary vacuum crystallizer to produce impure crystal which is recycled to the primary crystallizer with the iron-free aluminum nitrate solution. A small bleed stream is taken off at this point in the process to remove soluble impurities. This stream also contains a small amount of organic liquid, i.e., lost iron exchange, which can be skimmed from the liquid if properly arranged or passed to the disposal lagoon.

The iron-loaded organic phase leaving the extraction goes to a spray tower washing operation. There the small amount of nitrate which the DEHPA has removed from the aluminum nitrate aqueous phase is extracted completely by the water and discarded to the disposal lagoon, along with other solids and liquids. The nitrate-free, but cation impurity-containing organic phase then passes to a rubber-lined regeneration column where the organic liquid is contacted with aqueous HCl solution which strips the cations from the loaded organic. The regenerated organic phase then passes to a water-wash spray system where any small amount of contained hydrochloric acid is removed before recycle. Now the regenerated nitrate- and chloride-free liquid ion exchange organic is recycled for use again in the extraction area of the purification section.

The aqueous phase leaving the liquid ion exchange regeneration column is mixed with a small amount of H_2SO_4 in a reboiler of a Karbate HCl distillation column. A sulfate sludge containing sulfuric acid and ferrous sulfate waste material is removed from the bottom of the agitated reboiler of this still, while the overhead product (after condensation and partial reflux to the distillation column) is HCl of the proper concentration to be recycled for reuse in stripping-regeneration of the liquid ion exchange medium. The sludge is then removed from the bottom still and sent to the disposal lagoon. A small loss occurs at the liquid ion exchange medium, i.e., DEHPA, TBP, and kerosene. This loss is due to polymerization in the extractors, which have to be cleaned periodically and dumped or incinerated, if this is permissible. Other losses are due to the various solutions, e.g., the purified aluminum nitrate and the stripping solution in the liquid ion exchange regeneration.

In the case of organics lost to the purified aluminum nitrate solution, the organics would leave the system in the second crystallizer blowdown stream which, if properly designed, might permit skimming off the organic phase; alternatively the organics can be pumped to the disposal lagoon, along with the residue and other wastes. In the case of organics lost to the hydrochloric acid-stripping solution, they could be allowed to concentrate in this solution until the buildup became sufficient to skim off the separated phase.

(6) Decomposition

The purified aluminum nitrate crystals produced by the crystallization step are melted and then pumped as a 57% $Al(NO_3)_3$ solution into the three fluidized-bed hydrolysis reactors. These reactors are heated indirectly by means of a high-temperature, organic, heat-transfer medium through vertical tubes located in the reactor vessels. The heat-transfer medium is heated indirectly in separate furnaces directly fired by coal, or any other fossil fuel, depending on its cost and availability.

This heat-transfer medium consists of thermally stable, heavy, aromatic liquids contained in an entirely closed system. Over time, a small amount of cracking occurs and the resulting lower boiling liquids are bled from the system and replaced with new material. During the infrequent bleed-off operation, the liquids are condensed and ultimately used as fuel; the hydrocarbon gases would be banned, as they discharge from the condenser.

Since coal firing is used in this operation, provisions for fly ash removal and SO_2 control must be made if high-sulfur coal is used.

The fluid-bed reactors are arranged in parallel with regard to feed, and in series/parallel on the fluidizing vapor side to minimize the volume of initial fluidization vapor. The exit gas from the final two reactors passes through a set of cyclones and a glass cloth filter used to remove the small amount of alumina product elutriated from the beds in the form of a fine dust. The ratio of product which is formed on the surface of alumina particles which constitute the fluidized bed to the alumina product which leaves the reactor in the form of fine particles in the exhaust gas can be varied over a wide range by proper selection of the operating conditions of the system. Therefore, provision is made for the removal of prills, which are produced by accretion within the fluid bed, and their combination with the dust collected by the cyclone and glass cloth filter. It is important to understand that this reactor system is fluidized initially with steam and subsequently in the two parallel upper beds with steam and nitric acid vapor, i.e., no non-condensable gases. It is a hydrolysis that is occurring in this system, not a decomposition. This makes possible better recovery of nitrate values as condensable nitric acid, so that gaseous emissions of oxides of nitrogen are very small.

The product alumina material is then mixed with a stream of 1830°F alumina particles and the mixture is evenly distributed over the top layer of a packed moving-bed reactor system. In passage down through this second reactor, the remaining nitrate values (approximately 8% of the original nitrate) are liberated from the alumina particles in the form of nitric acid and nitrogen oxides. A small amount of steam purge is added to the bottom of the packed bed reactor to continually sweep the nitrogen oxides from the bed and to complete decomposition by the time the particles have reached the bottom of the system. The oxides of nitrogen that are purged from these operations with steam go to the nitric acid recovery system.

The solids outlet stream from the moving-bed reactor is passed over a vibrating screen to separate the fine alumina product particles from the coarser heat transfer medium. The coarser pebbles are conveyed to a packed moving-bed pebble heater in which they are reheated to 1830°F for the recycle again to the main bed decomposer.

(7) Nitric Acid Recovery

The nitric acid vapors evolved from the fluid-bed hydrolysis section are fed into a nitric acid concentrating tower. In view of the ubiquitous nature of chlorine in mineral deposits and process water, as well as the use of hydrochloric acid in the regeneration of DEHPA in this process, a means of removing the chloride from the main process stream, in addition to the one in the liquid ion exchange section, is required. This is done to ensure that corrosion of the materials of construction due to nitric acid is not accelerated by the presence of a high chloride level.

This chlorine is removed from the system by taking a relatively small side stream from the middle trays of the concentrating tower and passing it through a reactor into which air with a trace of ozone is bubbled. The ozone liberates free chlorine gas from the nitric acid water solution. The chlorine-free nitric acid can then be returned to the next tray of the distillation column. The resulting nitric acid goes to storage for subsequent recycle to the digestion section.

Chlorine gas liberated by the ozone is scrubbed with caustic in a vent scrubber. The nitrogen oxide leaving the moving-bed decomposer via the cyclone and cloth filters, mixed with water vapor, is passed through a condenser from which a large portion of the nitrogen oxide is recovered directly as nitric acid when it reacts with the water produced during condensation. The remaining nitrogen oxides, now rich in NO from the reaction between NO_2 and H_2O, are added to the gases leaving the ammonia burner in the nitric acid makeup plant. That combined gas stream goes to the absorption system for the production of makeup nitric acid for the system. Makeup nitric acid could be purchased or made from the oxidation of purchased ammonia. It is assumed that, in the latter alternative, any in-plant nitric acid unit would be equipped with pollution controls adequate to meet new stationary source standards.

(8) Final Calcination

The alumina leaving the final decomposer is sent to a well-insulated storage silo in which the phase transformation to alpha alumina occurs. This phase transformation is exothermic. The final calcined alpha-alumina is cooled to storage temperatures in a conventional facility used in Bayer alumina practice.

(9) Status of the Process

During the late 1960's Arthur D. Little, Inc. carried out a non-integrated, pilot-plant operation on the above-described nitric acid process. Moderate quantities were produced for inspection by an aluminum producer and, based on the chemical analysis of the product and consideration of the physical qualities, it was considered adequate in quality to be considered pot feed alumina for the Hall-Heroult process cells.

In 1975 the U.S. Bureau of Mines tested this process, among others, at its laboratory in Boulder City, Nevada. This test work, partly supported by the aluminum industry, was carried out at a so-called mini-plant (small integrated pilot plant). The results of this work have not yet been published.

(10) Effluent Controls

Water Pollution

The primary waste material from this process is the underflow from the series of thickeners, which consists of the acid insoluble clay fraction and a dilute aluminum nitrate aqueous solution having a concentration of approximately 50% solids, including the scrubber liquid effluent and liquid blowdown streams identified above that would go to the disposal lagoon.

Based on pilot plant data, the anticipated composition for this sludge stream (for the 700,000-ton/yr base case plant) follows:

Constituent	Quantity (ton/yr)
Al_2O_3	114
S_iO_2	3,392
$Al(NO_3)_3$ (soluble)	145
Other soluble nitrates, NO_3^- ions	164
Water	3,563
Other impurities	168
Total	7,546

The discharge, although smaller than that for the hydrochloric acid process, is still large and amounts to about 3.8 tons of waste material per ton of alumina produced, nearly 50% of which is water. The major kaolin clay reserves are in the states of Georgia (primarily), South Carolina, and Alabama. In these states the rainfall exceeds the evapo-transpiration rate, so that either water used for slurry transportation of the residues to the disposal lagoon would have to be eliminated, or recycle water from the disposal lagoons would have to be used. Ideally, recycle water from the disposal area should be used insofar as possible as process water makeup to the plant. However, the extent to which this can be accomplished is limited because of soluble impurities buildup, as discussed below. In addition to the three major components - alumina, silica, and iron oxides - the Georgia kaolins will contain small amounts of calcium, magnesium, titanium, sodium, potassium, manganese, phosphorus, zinc, lead, and a tiny amount of sulfur as sulfate, largely as calcium or magnesium sulfates, plus insoluble vanadium oxides. Considering the above, one would expect that soluble nitrates of calcium, magnesium, sodium, potassium, zinc, and lead might build up in any recycle loop. A small amount of phosphoric acid could also be present. Manganese would tend to follow the iron and would be present, along with iron, as sulfate sludge aqueous phase leaving the iron exchange regenerator column after treatment with sulfuric acid. Thus, overflow water from the disposal pond would be used to repulp the filter cake after the final washing thickener underflow filtration to provide slurry transport of the solids discharge to the disposal lagoon.

The pollutants of major concern are the soluble nitrates which include the above metal nitrates from the metals present in the clay. Because these wastes will be acidic and the liquid effluents will have a high total dissolved solid content, it is assumed that land disposal must be into an area where adequate provisions are made to prevent percolation into groundwater and run-off into surface water. The most probable methods for disposal are to either return the leached clays to the pits from which they were removed, or place them in specially designed above-ground impoundments. Although local geological conditions might permit return to the pits, it has been assumed that an above-ground, diked impoundment lined with an impervious liner, such as elastomer membrane, would be employed. Because the location of these alumina plants will be in geographical areas where the net rainfall exceeds the net evaporation, it will be necessary to institute a careful water management program with the process operation through recycle of water collected in the disposal lagoons. When a disposal lagoon is filled, it is expected that a ground cover would be implaced so as to prevent leaching and lateral transport of water from rainfall. This procedure creates a disposal cell in a form which should require the least long-term management and with the high probability that events, short of catastrophic happenings, would not cause the materials to enter the water environment.

It is estimated that the annual production of solid waste could be contained in an area 1,540 x 1,540 x 25 ft deep. The containing dikes would have inner and outer walls sloping at 45-deg angles and have a 40-ft wide roadway on the top. It is estimated that the construction costs for such an impoundment would be $1,810,000 (shown in Table IV-4), which is equivalent to $2.58/ton of alumina. Because of the more elaborate construction envisioned as necessary for impoundments holding these nitrate wastes than is necessary for Bayer process red-muds, the estimated solid waste disposal costs are significantly greater than the $0.48/ton of alumina from the Bayer process.

Air Pollution Considerations

The calcination of beneficiated clay pellets would not generate as much particulate as the calcination of bauxite, but dust emission controls will still be required for clay particulate as well as fly ash removal, since coal could be used in the calcination kiln. If high-sulfur coal is used, SO_2 scrubbing would also be required.

This process also generates several waste gas streams containing oxides of nitrogen. These are routed, manifolded, and lead to the acid recovery section. The acid recovery section has a small vapor purge line which must be scrubbed using dilute caustic; the resultant streams go to the tailings ponds.

Pollution Control Energy Use

Table IV-5 shows that pollution control energy consumption is much larger than for the other processes, largely because of the use of coal and necessity for stack gas scrubbing.

(11) Process Energy Use

This process consumes 139 kWh of power plus 25.30 x 10^6 Btu of fossil fuels, excluding the energy in the raw materials. Converted to a fossil fuel basis, i.e., including the inefficiencies in power generation, the total energy consumption amounts to 26.76 x 10^6 Btu/ton of alumina, which is considerably higher than for the Bayer alumina process in which total consumption on a fossil fuel basis is only 14.53 x 10^6 Btu/ton of alumina.

(12) Capital and Operating Cost

Capital cost estimates were originally made by Arthur D. Little, Inc. in 1973. These costs were checked in detail and in many cases revised by a major foreign aluminum producer who was interested in the process. These costs have been updated by appropriate escalation factors to early 1975 costs. The results check out reasonably close to the Bureau of Mines' estimates, revised and updated to the same time.

For a plant producing 700,000-ton/yr of alumina, we estimate that the capital costs would be $322 million, i.e., $460/annual ton of capacity.

The operating costs for a Georgia location based upon units costs, as of March 1975, are presented in Table IV-7. The estimated operating costs, including return on investment, add to $245/ton of alumina, which compares unfavorably with existing Bayer alumina plants that can presently produce alumina at $125/ton. This cost is about the same as that of new Bayer plants that produce alumina under present conditions at a cost of about $237/ton.

c. Toth Alumina Process

The Toth Aluminum Corporation (TAC) has been developing a process for the production of alumina and byproducts from clays and ferruginous bauxites. The process involves the chlorination of alumina-containing raw materials in the presence of carbon to produce aluminum chloride vapor and other volatile chlorides. These are subsequently purified to eliminate other metal chlorides and then oxidized to produce alumina and chlorine for recycle. It is proposed that the process would produce as byproduct a crude titanium dioxide which might be classed as rutile. Based on kaolin clays, the steps in the process involve: (1) ore drying and calcination; (2) chlorination in which the aluminum, titanium, and iron present in the ore are carried overhead as volatile chlorides; (3) separation of the chlorides from the aluminum chloride by fractional condensation and distillation; and (4) separate oxidation of the iron, silicon, and titanium chlorides to their respective oxides for recovery of chlorine for recycle. Finally, the aluminum chloride, after separation, is also oxidized to produce alumina and to recover chlorine for recycle. Details of the operation (see Figure IV-3) follow.

TABLE IV-7

ESTIMATED PRODUCTION COSTS FOR NEW ALUMINA PLANT, 1975
(Nitric Acid Leaching Process)

Product: Alumina
Process: Nitric Acid Leaching
Location: Georgia
Annual Capacity: 700,000 tons
Capital Investment: (CI) $322,000,000
Annual Production: 700,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
● Clay (Kaolin)	ton	2.50	3.83	9.58
● Nitric Acid	ton	90.00	0.148	13.32
● Hydrochloric Acid	ton	27.00	0.020	0.54
● DEHPA	lb	1.15	0.352	0.40
Energy				
● Purchased Fuel				
- Oil	10^6 Btu	1.85	1.30	2.41
- Coal	10^6 Btu	0.82	24.00	19.68
● Electric Power Purchased	kWh	0.015	139.00	2.09
● Misc				
Water				
● Process	10^3 gal	0.50	1.40	0.70
● Cooling	10^3 gal	0.05	84.00	4.20
Direct Operating Labor (Wages)	Man-hr	6.50	0.93	6.05
Direct Supervisory Wages	15% Op. Lbr.			0.91
Maintenance Labor (Wages)	Man-hr	6.75	0.98	6.37
Maintenance Supervision (Wages)	15% Mnt. Lbr.			0.96
Maintenance Materials	2% of CI			11.20
Labor Overhead	32% of wages			4.57
Misc. Variable Costs/Credits				
● Operating Supplies				0.87
TOTAL VARIABLE COSTS				83.85
FIXED COSTS				
Plant Overhead	60% of wages			8.57
Local Taxes and Insurance	2% of CI			9.20
Depreciation	7.1% of CI			32.66
TOTAL PRODUCTION COSTS				134.28
Return on Investment (pretax)	20% of CI			92.00
Pollution Control				19.00
TOTAL				245.28

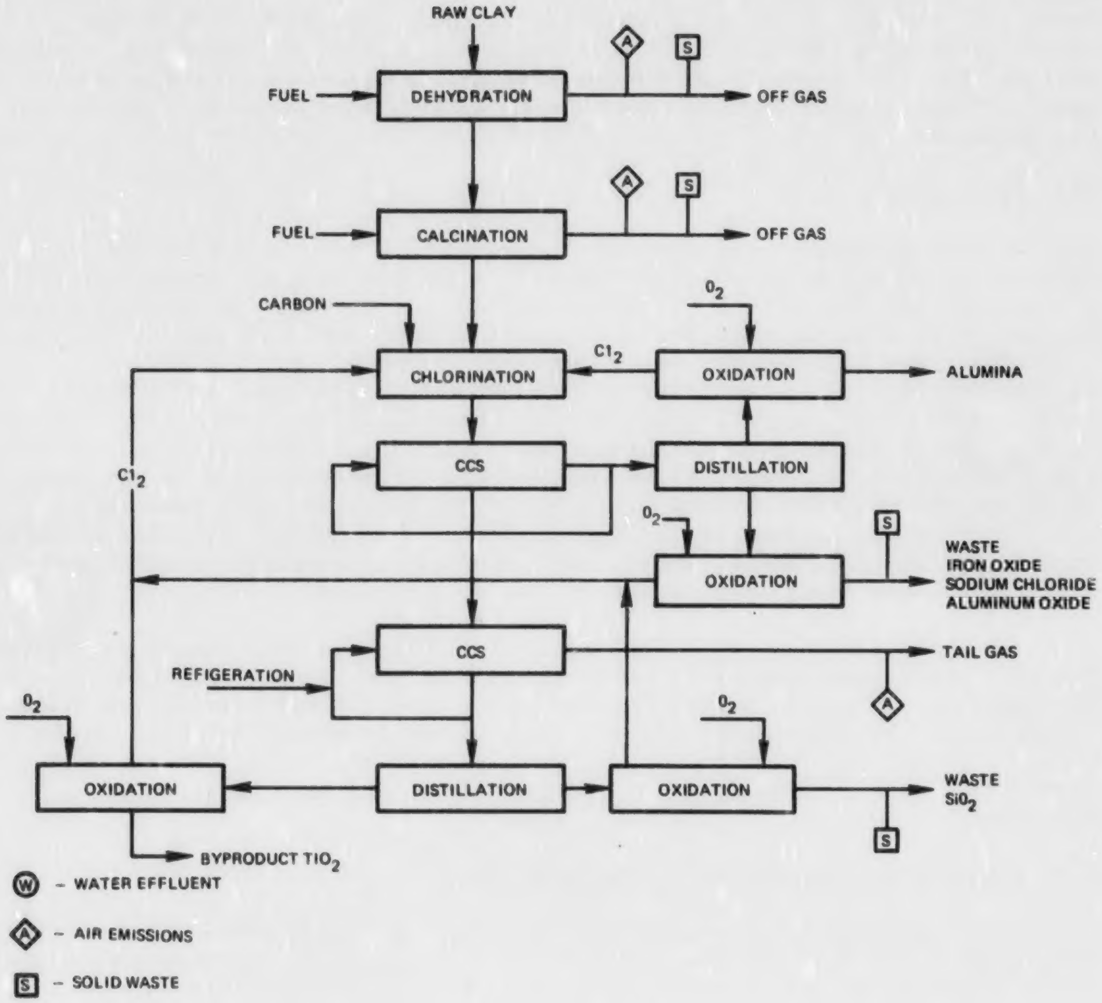
RAW CLAY
FUEL
DEHYDRATION
A
S
OFF GAS
FUEL
CALCINATION
A
S
OFF GAS
CARBON
O_2
Cl_2
CHLORINATION
OXIDATION
ALUMINA
CCS
DISTILLATION
Cl_2
O_2
S
OXIDATION
WASTE
IRON OXIDE
SODIUM CHLORIDE
ALUMINUM OXIDE
CCS
TAIL GAS
REFIGERATION
A
O_2
O_2
OXIDATION
DISTILLATION
OXIDATION
WASTE
SiO_2
S
BYPRODUCT TIO_2
W – WATER EFFLUENT
A – AIR EMISSIONS
S – SOLID WASTE

Figure IV-3. Toth Alumina Process

(1) Ore Drying and Calcination

The kaolin clay, which has a free moisture content of about 10%, is crushed and screened to pass 1/4-in. screen size. The screened ore is then dried, presumably in kilns or fluid-bed dryers operated at about 300°F. The dried ore, still containing 5% moisture, is then calcined at 1290°F and discharged hot to the chlorination reactors. All of these operations require devices that will prevent the discharge of fine particulate to the environment. If high-sulfur fuel is used, the facilities have to be able to control SO_2 emissions.

(2) Chlorination

In this operation, calcined ore is fed at 1290°F to fluidized bed chlorinators operating at 1470°-1830°F where, in the presence of carbon, the ore is chlorinated. The carbon can be petroleum coke or low-grade coal coked at the lowest cost as the reducing agent. Chlorine to the chlorinators is primarily recycled off-gas from the aluminum chloride, ferric chloride, titanium tetrachloride, and silicon tetrachloride oxidations, and possibly could contain some oxygen and nitrogen. Makeup chlorine is obviously required as a result of losses from the system which amount to almost 2% of the chlorine circulation. TAC has carried out its own research on this step in the operation, but it should be pointed out that commercial plants have been successfully operated to produce aluminum chloride and other metal chlorides by chlorination in the presence of carbon under thermal and corrosive conditions similar to those found in this step of the Toth process.

TAC indicates that the chlorination of silicon and iron can be suppressed, but we believe that some iron, silicon, and even some sodium chloride is carried over in the off-gases. TAC indicates that the net overall reactions occurring in the chlorinator are endothermic, but proposes that heat can be added by preheating the chlorine, and that part of the carbon present can be burned to carbon dioxide by air or oxygen addition to make up any heat deficiency.

(3) Recovery and Separation of the Chlorides

Chlorides that pass overhead are separated by a combination of fractional condensation and distillation, followed by reoxidation of the separated fractions. The temperature of the off-gas from the chlorinator falls between 1470° and 1830°F. These gases are first cooled indirectly in a waste heat boiler to about 480°F. The cooled gas stream is then scrubbed with recycled sodium chloride-aluminum chloride-ferric chloride molten salt solvent at 300°F to remove aluminum chloride and ferric chloride and any sodium chloride in the gas stream. Thus, the remaining gas off the scrubber contains titanium tetrachloride, silicon tetrachloride, and non-condensable gases--carbon monoxide and carbon dioxide. Since carbon and reactants (titania, aluminum, silica, and iron) are always in excess, there would be little if any chlorine breakthrough.

The aluminum chloride, ferric chloride, and sodium chloride removed in the scrubber are then passed to a distillation column operated under pressure wherein the absorbed aluminum chloride and ferric chloride are separated by distillation. Sodium chloride condensed in the scrubber is bled from the system at this point, carrying with it some aluminum chloride and iron chloride which is oxidized in a separate unit to iron oxide and aluminum oxide, while the sodium chloride remains unchanged. This operation produces chlorine for recycle, while the solids are discharged to disposal.

The aluminum chloride-ferric chloride vapors from the distillation column are then fed to a second distillation column, also operating under pressure, for the final separation of aluminum chloride and ferric chloride. The aluminum chloride separated at this point is the product stream which is subsequently oxidized to produce the product alumina and recycle chlorine. Ferric chloride produced at the bottom of this column can be sold directly, or can be sent to an oxidizer to recover the chlorine for recycle and oxides of iron.

(4) Aluminum Chloride Oxidation

Liquid aluminum chloride, the main product stream from the distillation column, is vaporized with the vapor then oxidized in fluid-bed oxidizers operated at about 1500°-1560°F. Oxidation is carried out with oxygen to avoid contamination of the recycle chlorine with nitrogen. The oxidizer off-gas is passed through cyclone separators for removal of solids. The off-gas, essentially chlorine, is recycled back to the chlorinator.

(5) Titanium Tetrachloride and Silicon Tetrachloride Separation and Treatment

Off-gases from the aluminum chloride, iron chloride scrubber, which consist essentially of titanium tetrachloride, silicon tetrachloride, carbon monoxide, and carbon dioxide, enter refrigerated condensers where the titanium tetrachloride and silicon tetrachloride are condensed at about -22°F. Silicon tetrachloride and titanium tetrachloride from this condenser are fed to a distillation column for separation of the components. Separated chlorides from the distillation column are oxidized to recover chlorine for recycle. TAC is proposing to produce special silicas for sale, which may or may not be possible. However, the oxidized titanium tetrachloride would be a crude titanium dioxide which certainly could be sold. This crude TiO_2 byproduct would be equivalent in value to rutile.

(6) Current Status

This process is presently under development by the Toth Aluminum Corporation. The development work is being carried out on a small scale. We know of no plans to build a large pilot plant, although TAC is actively promoting and seeking sponsors for such a plant that would be designed to produce 90 ton/day of alumina. It is expected that this pilot plant would be supported by the sale of byproduct crude titanium dioxide and special silicas produced from the oxidation of titanium tetrachloride and silicon tetrachloride.

(7) Effluent Control

Water

This is a dry process. The scrubbing media used are molten salt mixtures that are products of the process and are subsequently separated. There are no aqueous effluent process streams, except indirect cooling water requirements for cooling of exothermic reactions. Thus, cooling tower blowdown is probably most economically handled by treating it; costs are estimated in Table IV-8.

Air Pollution Considerations

Three potential emission streams (described below) are apparent from this technology:

(a) The exhaust from the chlorinator, after cooling and scrubbing to remove the chlorides, will contain CO, CO_2, and probably traces of HCl, if moisture, chlorine, the more volatile titanium, and silicon tetrachlorides are present. We expect that some chlorinated hydrocarbons would result from the chlorination of heavy volatile material remaining in the coke. We would also expect that these materials would be removed in the low-temperature condensation step required to remove the titanium and silica tetrachlorides. When these materials are oxidized to recover the chlorine values for recycle, the chlorinated hydrocarbons are also destroyed at the high-temperature conditions where these materials oxidize.

(b) The dry residue from the chlorinator contains the ash from the clay and coke, alumina, and non-volatile chlorides of the alkali and alkali earth metals present in the clay and coke ash.

(c) In separating alumina from $AlCl_3$ vapor and chlorine following oxidation, residual chlorine and $AlCl_3$ may exit in the solid alumina. The same may also occur in the oxidation of silicon and titanium tetrachlorides.

We have assumed that the sources of chlorine emission would be controlled because there is a real economic incentive to conserve it and to prevent escape of this hazardous gas, although it is not a criteria pollutant.

The emission rates for this process depend upon purge and exhaust rates which for the most part are unknown at present.

In a series of enclosed condensing and scrubbing steps, each of the chloride constituents is removed, leaving an exhaust containing carbon monoxide, carbon dioxide, hydrogen chloride, chlorine and potentially sulfur-containing gases such as H_2S, COS, etc. This stream could be burned in a CO boiler and then caustic scrubbed to remove hydrogen chloride or sulfur dioxide. Estimated costs for air pollution control are shown in Table IV-9.

TABLE IV-8

TOTH CHLORINATION PROCESS
COOLING TOWER BLOWDOWN WASTEWATER TREATMENT COSTS
(Basis: 700,000-ton/yr alumina production)

CAPITAL INVESTMENT - $355,000

	Annual Quantity	Cost per Unit Quantity	Annual Cost
VARIABLE COSTS			
Operating Labor (including suprvis + OHD)	1,800 man-hr/yr	$11.38/man-hr	20,485
Maintenance (including labor + OHD)	-	-	-
Chemicals			
• Sulfur Dioxide	68 ton/yr	$340/ton	23,120
• Lime	72 ton/yr	$30.75/ton	2,215
• Sulfuric Acid	34 ton/yr	$51.15/ton	1,740
Fuel	-	-	-
Electrical Power	48,300 kWh/yr	0.012/kWh	580
Sludge Disposal	675 ton/yr (@ 10% solids)	$5.00/ton	3,375
TOTAL VARIABLE COST			51,515
FIXED COST			
Taxes & Insurance (@ 2%)	-	-	7,100
Depreciation (@ 7.1%)	-	-	25,205
TOTAL FIXED COST			32,305
TOTAL ANNUAL COST			83,820
RETURN ON INVESTMENT @ 20%			71,000
TOTAL			154,820
$ per ton of alumina			0.22

Notes: 1. Treatment costs are based on a cooling tower blowdown flow rate of 0.9 10^6 gal/day (2% blowdown) and a chromium concentration of 30 mg/l.

2. Treatment consists of reduction followed by lime precipitation and clarification.

TABLE IV-9

AIR POLLUTION CONTROL COSTS FOR THE TOTH ALUMINA PROCESS

	Units Used in Costing or Annual Cost Basis	$/Unit	SO_2 Control	HCl Control
CAPITAL INVESTMENT (CI)			$6,588,000	$276,000
VARIABLE COSTS ($/yr)				
Electric Power Purchased	kWh	0.012	170,200	2,700
Labor Wages	man-hr	6.50	86,000	16,000
Supervisory Wages	15% labor		12,900	240
Maintenance, Labor, Supervision, Materials and Supplies	5% CI		329,400	13,800
Labor Overhead	32% wages		31,600	590
Chemicals				
• Lime	ton	30.75	1,724,700	
• Soda Ash				130,300
Residue Disposal	ton	5.00	455,500	--
Total			2,810,300	163,630
FIXED COSTS ($/yr)				
Plant Overhead	60% wages		59,300	1,100
Local Taxes and Insurance	2% CI		131,800	5,520
Depreciation	CI/14		470,600	19,700
TOTAL PRODUCTION COSTS				
Return on Investment (pretax)	20% CI		1,317,600	55,200
TOTAL ($/yr)			4,789,600	230,750
TOTAL ($ per ton alumina)			$6.84	$0.33

Two solids streams require flushing to remove the chlorides. The chlorinator purge is large, because the clay and coke ash must be rejected. Also, the alumina formed in the oxygenator has to be flushed. The exhaust containing the flushing agent (air, for example) and residual chlorine is scrubbed, along with the flush exhaust from the chlorinator purge, and subsequently is scrubbed again with caustic or lime.

Solid Waste and Liquid Waste Control

The major sources of solid wastes are the discharge of inert material from the chlorinator and solid wastes from the sodium chloride purge, which contain iron chloride and some aluminum chloride, along with the sodium chloride. This stream is oxidized to recover chlorine from the iron and aluminum chlorides, leaving iron oxide, alumina, and sodium chloride as solid wastes. This could be leached to remove the sodium chloride in a waste liquid stream, but only if the alumina could be recovered for recycle by subsequently removing the iron oxide by magnetic separation. The third potential waste solids stream is the silica resulting from the oxidation of silicon tetrachloride.

All of these streams are likely to contain some soluble chlorides. These materials could be removed as dry solids, but the soluble chlorides would be eventually leached by rain into the groundwater.

Probably the best way to handle such solid waste materials, along with discharges from any caustic or lime scrubbers used to control chlorine or hydrogen chloride emissions, is to dispose of these solid and liquid effluents in a storage area or lagoon lined with an impervious elastomer membrane.

Our best estimate of the composition and volume of these liquid and solid waste materials for a 700,000-ton/yr alumina production are as follows:

Constituent	Quantity (ton/day)
Al_2O_3	218
S_1O_2	2,694
Fe_2O_3	31
Other	30
Soluble Chlorides, Cl^-	80
Water	600
Total	3,653

This discharge is smaller than that for the acid leaching processes, amounting to only 1.8 tons of waste per ton of alumina, because the waste is largely a dry material. Again, the most likely location for a clay-based alumina plant would be in the kaolin belt of Georgia (primarily), South Carolina, or Alabama. In these states the rainfall exceeds evapo-transpiration so that water used for slurry transportation of the residue to the disposal pond would have to be eliminated, or recycle water from the disposal lagoons would have to be used. Ideally, recycle water from the disposal area should be used as process water makeup to the plant. However, the extent to which this could be accomplished is limited because of soluble impurities buildup, as discussed below.

In addition to the major components - silica, alumina, and iron oxides - the kaolin clays contain small amounts of calcium, magnesium, titanium, sodium, potassium, manganese, phosphorus, zinc, lead, and tiny amounts of sulfur as sulfate, largely as calcium sulfate, plus a small amount of vanadium as oxide. Of these impurities it can be expected that the chlorides of calcium, magnesium, sodium, potassium, lead, and manganese would remain largely in the residue from the chlorination, or be separated out in the first condenser and be separated from the aluminum chloride and ferric chloride in the first distillation discharged with the higher boiling sodium chloride-containing fraction. The vanadium tetrachloride separates out with the titanium tetrachloride. The phosphorus separates as the trichloride with the silicon tetrachloride. The vanadium remains as an oxide contaminant in the titanium dioxide. The phosphorus contained in the silicon tetrachloride volatilizes as oxide during the oxidation of the silicon tetrachloride to silica to recover chlorine for recycle. Therefore, the chlorine-containing off-gases from the silicon tetrachloride oxidation have to be scrubbed with water to recover the P_2O_5 as phosphoric acid for disposal.

Thus, a variety of soluble chlorides are present in the solid and liquid waste streams to the disposal lagoon which build up in the system if water from the lagoon is used as process makeup. The clarified water from the lagoon, however, could be used to provide slurry transport of solids to the disposal lagoon.

The pollutants of major concern are the soluble chlorides discussed above. The wastes are acidic and the effluent, if transported by water slurry to the disposal area, would contain a high total dissolved solids content. It is assumed that land disposal would have to be made into an area where adequate provisions are made to prevent percolation into groundwater and run-off into surface water.

The most likely method for disposal is either to return the effluents to the mined-out areas, or place them in specially designed above-ground impoundments lined with an impervious liner, such as an elastomer membrane. When a disposal lagoon is filled, it is expected that a ground cover would be implaced so as to prevent leaching and lateral transport of water from rainfall. This procedure would create a disposal cell in a form that would require the least long-term management and with the high probability that events, short of a catastrophic happening, would not cause the materials to enter the water environment.

It is estimated that the annual production of solid wastes could be contained in an area 1,370 x 1,370 x 25 ft deep. The containing dikes would have inner and outer walls sloping at 45-deg angles and have a 40-ft wide roadway on the top. It is estimated that the construction costs for such an impoundment would be \$1,444,000 shown in Table IV-4, which is equivalent to \$2.06/ton of alumina. Because of the more elaborate construction envisioned as necessary for impoundment holding of those chloride wastes than is necessary for the Bayer process red-muds, the estimated solid waste disposal costs are significantly greater than the \$0.48 per ton of alumina from the Bayer process.

Pollution Control Energy

Table IV-5 shows that pollution control energy requirements of about 0.3 x 10^6 Btu/ton of alumina are much larger than for the Bayer process, but still small compared with process energy requirements.

(8) Process Energy Use

This process consumes 333 kWh of power and 25.1 x 10^6 Btu of fossil fuel, excluding the energy in the raw material. Converted to a fossil fuel basis, i.e., considering the inefficiencies in power generation, the total consumption amounts to 28.59 x 10^6 Btu/ton of alumina. This is considerably higher than the Bayer process in which total energy consumption on a fossil fuel basis is only 14.53 x 10^6 Btu/ton of alumina.

(9) Capital and Operating Costs

The capital and operating costs are based on estimates made by Toth Aluminum Corporation. We have checked the operating cost unit requirements and unit costs. The unit requirements are consistent with those reported by others for similar operations, i.e., from the production of aluminum chloride and titanium tetrachloride. The capital costs are also based upon information from TAC estimates for the first quarter of 1975 to which we have added a small contingency. The resulting capital cost estimates are for a plant based on the above-described process. Toth Aluminum Corporation estimated it would cost $205/annual ton of capacity. The estimate used in the analysis is based on $331/annual ton of capacity. This would mean that the capital costs would be lower than for a Bayer plant which for 700,000-ton/yr capacity would cost $400/annual tons today.

The estimated operating cost per ton of alumina (including return on investment) based on this process is shown in Table IV-10 to be $190.09/ton of alumina with a credit for the byproduct titania produced and about $209 without the credit for byproduct titania. These estimated costs with byproduct credit are higher than from existing Bayer alumina plants, presently estimated to produce alumina at $125/ton and which are expected to feel the effects of increasing bauxite costs. However, these costs compare very favorably with estimates for producing alumina in any new Bayer plant installation in the United States, expected to be about $237/ton of alumina.

d. Summary of Production Costs and Energy Requirements for Production of Alumina

Table IV-11 summarizes the costs and the energy consumption (fossil fuel basis) for producing alumina by the existing Bayer process and the alternative hydrochloric acid and nitric acid clay leaching processes and the Toth chloride alumina process based on clay as the raw material. These costs are compared on the basis of new plants, since it is unrealistic to compare these new process plants with existing Bayer plants which are largely depreciated.

TABLE IV-10

ESTIMATED PRODUCTION COSTS FOR NEW ALUMINA PLANT, 1975
(Clay Chlorination - Toth)

Product: Alumina
Process: Clay Chlorination: Toth
Location: Texas or Georgia

Annual Capacity: 700,000 tons
Capital Investment: (CI) $232,600,000
Annual Production: 700,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
● Clay (Kaolin)	ton	2.50	3.00	7.50
● Chlorine	ton	125.00	0.04	5.00
● Oxygen	ton	12.00	1.31	15.72
Byproduct Credits (Crude TiO_2)	ton	332.00	0.058	-19.26
Energy				
● Purchased Fuel				
- Coal	10^6 Btu	0.82	8.45	6.93
- Coke	ton	35.00	0.64	22.40
● Electric Power Purchased	kWh	0.015	333.00	5.00
● Misc.				
Water				
● Process	10^3 gal	0.50	0.80	0.40
● Cooling	10^3 gal	0.05	20.25	1.01
Direct Operating Labor (Wages)	Man-hr	6.50	0.72	4.68
Direct Supervisory Wages	15% Op. Lbr.			0.70
Maintenance Labor (Wages)	Man-hr	6.75	1.05	6.83
Maintenance Supervision (Wages)	15% Mnt. Lbr.			1.02
Maintenance Materials	2% of CI			6.62
Labor Overhead	32% of wages			4.23
Misc. Variable Costs/Credits				
● Other Operating Supplies				5.90
TOTAL VARIABLE COSTS				74.68
FIXED COSTS				
Plant Overhead	60% of wages			7.94
Local Taxes and Insurance	2% of CI			6.62
Depreciation	7.1% of CI			23.59
TOTAL PRODUCTION COSTS				112.83
Return on Investment (pretax)	20% of CI			66.46
Pollution Control				10.80
TOTAL				190.09

TABLE IV-11

COMPARATIVE COSTS AND ENERGY CONSUMPTION IN THE ALUMINA INDUSTRY
Base Line: Bayer Process

	Variable and Fixed Costs $/Net Ton			
	New Bayer	Hydrochloric Acid Leaching	Nitric Acid Leaching	Toth Alumina
Total for process*	235.37	320.72	226.28	179.29
Pollution control*	1.40	5.00	19.00	10.80
TOTAL	236.77	325.72	245.28	190.09

	Energy Consumption 10^6 Btu/Net Ton			
	New Bayer	Hydrochloric Acid Leaching	Nitric Acid Leaching	Toth Alumina
Total production	14.53	39.21	26.76	28.59
Pollution control	0.06	0.02	0.70	0.29
TOTAL	14.59	39.23	27.46	28.88

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*Includes return on investment

B. ALUMINUM PRODUCTION

1. Status

The alternative processes for the production of aluminum that are being considered by the aluminum industry are those methods that will significantly reduce the power consumption in the Hall-Heroult electrolytic reduction process, which is presently used to produce all of the primary aluminum throughout the world.

The matter of greatest concern to the aluminum producers in the United States is the amount of power consumed in smelting alumina to aluminum in the existing aluminum plants. This is a critical matter in view of the rising cost of energy and power both in the United States and Europe. Historically, because of the large amount of power consumed in the conversion of alumina to aluminum, the industry has been located near sources of low-cost power. Within the United States such sources are becoming harder to find. Unless power consumption can be reduced, the growth in aluminum production in the United States will be slower in the future.

As a result of this concern, Alcoa has developed a new aluminum chloride electrolysis process that is expected to require less power than the present Hall-Heroult process. This process is to be based on Bayer alumina converted to aluminum chloride. One might ask why not on alumina recovered as aluminum chloride from clays by the Toth alumina process. The answer is that this would present a logistics problem with respect to recycling chlorine from the Alcoa chloride cells that would be required for the chlorination of clays to produce aluminum chloride. Since it is costly to ship chlorine from the aluminum plant to the sources of the clay or clay to the aluminum plant, the only potential application of these two processes in combination would be to locate aluminum plants at the source of the clays. Unfortunately, low-cost power is not generally available in these areas. Moreover, to do this would mean concentrating the new aluminum plants near sources of clay which would limit the application of this new technology to new plants. However, we have considered the potential of this combination of the Alcoa process and Toth alumina processes because it is possible that in the longer range future a few aluminum plants might be located at the clay raw material sources. We believe that this is not likely to happen in the near future because of the momentum that is represented by the large existing system in the aluminum industry which, for a long time, will continue to be based on imported alumina or bauxite converted to alumina in domestic Bayer alumina plants. Also the production of alumina benefits from the scale of operations, i.e., normally one alumina plant produces enough alumina to supply several smelters so that it is likely to be more costly to match the size of the raw material recovery plant, in this case aluminum chloride from clay, to that required for a single nominal-sized aluminum smelter.

In addition to interest in the new Alcoa process, the U.S. aluminum industry is showing renewed interest in the potential of so-called refractory hard metal cathodes for reducing power consumption in the present Hall-Heroult aluminum reduction cells. Therefore, we have considered this renewed development because it represents an opportunity to retrofit cells in existing plants to conserve energy.

The Toth aluminum process has received a great deal of publicity. This is not the Toth alumina from clay process described earlier, but another process that has been under development by TAC for converting aluminum chloride to aluminum metal. It represents a major departure from the production of aluminum by electrolysis to a pyrometallurgical process. In the past, the aluminum producers have been interested in pyrometallurgical methods of producing aluminum, but have shelved these older concepts, such as the Gross process on which Alcoa spent a great deal of money and time. Also, Pechiney worked on two pyrometallurgical processing methods that have long since been shelved. The Toth aluminum process is the latest of these pyrometallurgical processes, and it is the only one that has generated any current interest; therefore, it is considered in this report.

We have, therefore, evaluated four alternative process options for aluminum production: 1) Alcoa chloride process, 2) Refractory hard metal cathodes, 3) Toth aluminum process, and 4) the combination of the Toth alumina process producing aluminum chloride from clay as feed to the Alcoa chloride process.

2. Current U.S. Aluminum Technology (Hall-Heroult Process)

The existing technology for the production of aluminum is at present entirely the Hall-Heroult electrolytic reduction process, discussed in detail in Appendix B. This process is old and well developed, but is applicable only to alumina as the raw material. While there are some variations in U.S. aluminum smelters as regards the size and amperage-carrying capacity of the cells and the older Soderberg modification method of producing and consuming anode carbon, the process used is basically the same Hall-Heroult method.

a. Costs

Average cost of aluminum produced from existing U.S. aluminum smelters is estimated to be about $742/short ton of aluminum (see Table IV-12). Capital costs for new Hall-Heroult aluminum smelter capacity as of March 1975 was about $1750/annual ton of aluminum capacity (see Table IV-13). The nominal size of a conventional aluminum smelter would be about 160,000 short ton/yr, which is about average for the present smelters in the U.S. industry. Capital investment today for this size installation would be about $280 million. Present costs for aluminum produced from new Hall-Heroult smelter installations, including return on investment, would be $1,181/short ton.

b. Process Energy Consumption

The average energy consumption in Hall-Heroult aluminum smelters in the United States is 15,600 kWh/ton with new plants projecting 12,000 kWh. In addition, 24×10^6 Btu of fossil fuel are required per ton of aluminum. On a fossil fuel basis, i.e., considering the inefficiencies of power generation, the total energy consumption would be 187.8×10^6 Btu/ton of aluminum for old plants and 150×10^6 Btu/ton for new facilities, not including the energy inputs in the raw or consumable materials.

TABLE IV-12

ESTIMATED PRODUCTION COSTS IN PRESENT DAY ALUMINUM PLANTS, 1975
(Hall Process)

Product: Aluminum
Process: Hall
Location: Kentucky - Tennessee
Annual Capacity: 160,000 tons
Capital Investment(CI): *
Annual Production: 160,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
• Bayer Alumina	Net ton	125.00	1.93	241.25
• Cryolite	Net ton	336.00	.035	11.76
• Aluminum Fluoride	Net ton	350.00	.02	7.00
Energy				
• Purchased Fuel				
- Natural Gas	10^6 Btu	1.50	6.6	9.90
• Calcined Coke	Net ton	80.00	.52	41.60
• Pitch	Net ton	70.60	.15	10.60
• Electric Power Purchased	kWh	0.01	15,600.	156.00
• Misc.				
Water				
• Process				
• Cooling				
Direct Operating Labor (Wages)	Man-hr	6.50	3.5	22.75
Direct Supervisory Wages	15% of Op. Lbr.			3.41
Maintenance Labor (Wages)	Man-hr	6.50	4.5	29.25
Maintenance Supervision (Wages)	15% of Mnt. Lbr.			4.38
Maintenance Materials	2.5% of RC			43.75
Labor Overhead	32% of wages			19.13
Miscellaneous Variable Costs/ Credits				
TOTAL VARIABLE COST				600.78
FIXED COST				
Plant Overhead	60% of wages			35.87
Local Taxes and Insurance	2% of UI			17.50
TOTAL PRODUCTION COSTS				654.15
Capital charges	5% of UI			43.75
Pollution Control				44.00
TOTAL ($/ton)				741.90
TOTAL ($/lb)				0.37

*Est. Avg. Undepreciated Investment (UI) $140,000,000
1975 Replacement Cost (RC) $280,000,000

TABLE IV-13

ESTIMATED PRODUCTION COSTS IN NEW ALUMINUM PLANTS, 1975
(Hall Process)

Product: Aluminum

Process: Hall

Location: Tennessee - Kentucky

Annual Capacity: 160,000 tons

Capital Investment (CI)*: $280,000,000

Annual Production: 160,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
• Bayer Alumina	ton	125.00	1.93	241.25
• Cryolite	ton	336.00	.035	11.76
• Aluminum Fluoride	ton	350.00	.02	7.00
Energy				
• Purchased Fuel				
- Natural Gas	10^6 Btu	2.00	6.60	13.20
• Calcined Coke	ton	80.00	.52	41.60
• Pitch	ton	70.60	.15	10.59
• Electric Power Purchased	kWh	0.012	12,000.00	144.00
• Miscellaneous				
Water				
• Process				
• Cooling				
Direct Operating Labor (Wages)	Man-hr	6.50	3.50	22.75
Direct Supervisory Wages	15% Op. Lbr.			3.41
Maintenance Labor (Wages)	Man-hr	6.50	4.50	29.25
Maintenance Supervision (Wages)	15% Mnt. Lbr.			4.39
Maintenance Materials	2.5% of CI			43.75
Labor Overhead	32% of wages			19.14
Miscellaneous Variable Costs/ Credits				
TOTAL VARIABLE COSTS				592.09
FIXED COSTS				
Plant Overhead	60% of wages			35.88
Local Taxes and Insurance	2% of CI			35.00
Depreciation	7.1% of CI			124.25
TOTAL PRODUCTION COSTS				787.22
Return of Investment (pretax)	20% of CI			350.00
Pollution Control				44.00
TOTAL				1,181.22

c. Effluent Control

(1) Air and Water

Details of effluent control for the Hall-Heroult aluminum smelters are discussed in Appendix C. Below the situation is described with respect to water, air, and solids contained therein.

The principal sources of wastewater from primary aluminum smelting are effluents from wet scrubbers used on pot line and pot room ventilation, wet scrubbers used on anode-baking furnace flue gas, and wet scrubbers used on cast house off-gases. There is also cooling water used in casting, cooling rectifiers, and boiler blowdown. The volume of these sources of wastewater is related to the type of air pollution control system used for particulate and fluoride control. If dry gas cleaning methods are used in which the alumina ultimately fed to the cells is the absorbent used to remove pollutants from pot room gas, there would be no fluoride-containing wastewater from pot lines and pot rooms. However, the ability to use dry scrubbing methods, i.e., alumina to recover fluorides and particulates, depends on crust-breaking procedures for charging alumina feed to the pots. If the center crust-breaking is used, i.e., breaking the crust along the center line of the cell, then the cell can be tightly hooded and dry scrubbing used. If side-breaking technology is used, it is more difficult to hood the cell tightly and, with secondary air inflow, the choice is wet scrubbing. Side-crust breaking and alumina feeding result in higher electrical efficiency relative to center-crust breaking and are therefore the logical choices for energy conservation in the future. At present, this method is less amenable to tight hooding and thus requires wet scrubbing.

(2) Solid Waste

Minor amounts of solid wastes originate from handling the storage and feeding raw and consumable materials (alumina, calcined coke, cryolite and aluminum fluoride) brought into the smelter. Emissions of these materials are largely in the form of dust from handling and feeding to the cells and to the anode-making operations.

However, rebuilding of cells is the major source of solid waste from an aluminum smelter. When a cell reaches the end of its useful life and has to be rebuilt, it is removed from the line and taken to the cell-reconditioning shop where the old refractory lining, remaining cathode, and steel connector bar are removed. The cell is then completely dismantled and rebuilt. This operation generates a good deal of solid rubble and waste solid materials. Most of the refractory internals are impregnated with cryolite and aluminum fluoride. These materials are typically leached to recover the fluorides for reuse, before discharging the resulting inert refractory wastes to a suitable disposal site. The resulting leach solution is subsequently treated to recover the fluorides for reuse.

For a complete control system for an aluminum smelter with a capacity of 160,000 ton/yr investments would be about $178 per annual ton of aluminum capacity for a prebake plant. Consequently, for a 160,000 ton/yr aluminum smelter, the investment would amount to $28.48 million as summarized in Table IV-14. Operating costs would be about $58 and, with an allowance for chemical recovery, the net cost per ton of aluminum would be about $44 as shown in Table IV-15.

(3) Pollution Control Energy

Table IV-16 shows energy requirements for pollution control to be about 1.7×10^6 Btu/ton aluminum.

3. Alternative Aluminum Production Processes

a. Alcoa Chloride Process

Alcoa announced its new electrolytic chloride process for aluminum smelting in 1973 with plans for a 15,000 ton/yr demonstration unit to be built in Palestine, Texas for a 1976 startup. However, it has not released much detail publicly. We base our estimates on what we can surmise from its announcements, on a review of the pertinent patents, on a review of the literature on chlorination of aluminum ores, and on a consideration of possible temperatures and compositions. We have compared the process with the existing Hall oxide electrolytic route for producing aluminum from alumina, described briefly above and in Appendix A.

Briefly, the Alcoa chloride process starts with pot feed alumina from the Bayer process. Specifications call for a minimum purity of 99.426% alumina. The limits on impurities are: SiO_2 - .025%; Fe_2O_3 - .03%; CaO - .06%; MgO - .002%; NiO - .005%; CaO - .01%; MnO_2 - .002%; Na_2O - .4%; TiO_2 - .005%; ZnO - .02%; V_2O_5 - .002%; Cr_2O_3 - .002%; K_2O - .005%; Li_2O - .001%; and P_2O_5 - .005%. This alumina is converted into aluminum chloride by chlorination in the presence of carbon to form volatile aluminum chloride. This, in turn, is purified and fed to the electrolytic cells to produce molten aluminum at the cathode and chlorine at the anode. The chlorine is recycled to the chlorination system. Figure IV-4 presents our judgments of how the Alcoa process is being designed to operate. The various steps in the operation of the Alcoa process shown in Figure IV-4 are described below.

(1) Coking

While alumina is fed to the top stage of a two-stage, fluid-bed coking system, No. 6 fuel oil is fed to the bottom stage where it is coked to impregnate carbon on the alumina. The top fluid-bed stage is operated at relatively low temperatures to condense uncracked liquid hydrocarbons that come overhead from the lower stage and to separate these condensable liquids from the noncondensable gases. The top stage is equipped with cooling pipes inserted in the bed to maintain a low temperature. The condensed, cracked hydrocarbon liquids coat the aluminum particles.

The alumina then flows to the bottom fluid-bed stage, operated at 1,650°F, where the fuel oil is cracked and coked. About 70% of the carbon contained in

TABLE IV-14

CAPITAL INVESTMENT SUMMARY FOR ENVIRONMENTAL CONTROL IN ALUMINUM INDUSTRY

Base line: Hall-Heroult Cells for Aluminum
Bayer Process for Alumina

	Base line	Alternative Process		Combination Processes	
		Existing Hall with TiB_2 Cathodes	New Alcoa $AlCl_3$	Toth Clay-ALCOA Chloride	Bayer-Hall/Heroult
Production basis, ton/yr aluminum	160,000	208,000	160,000	160,000	160,000
Water and/or Solids Pollution Control Investments ($000)	- *	- *	375	595	- *
Air Pollution Control Investments ($000)					
Particulates	-	-	-	813	390
SO_2 control	-	-	3,700	10,613	-
HCl control	-	-	155	322	-
Fluoride	28,480 *	29,900 *	-	-	28,480 *
TOTAL ($000)	28,480 *	29,900 *	4,230	12,343	28,870 *

Source: Arthur D. Little, Inc. estimates

*All air, water, and solids pollution control costs in aluminum production are provided in this number.

TABLE IV-15

ANNUAL OPERATING COST SUMMARY FOR ENVIRONMENTAL CONTROL IN ALUMINUM INDUSTRY
Base line: Hall-Heroult Cells for Aluminum
Bayer Process for Alumina

	Base line	Alternative Process		Combination Alternative Processes	
		Existing Hall with TiB_2 Cathodes	New ALCOA Chloride	Toth Clay-ALCOA Chloride	Bayer-Hall/Heroult
Production basis, ton/yr	160,000	208,000	160,000	160,000	160,000
Water and/or Solids Pollution Control Costs ($000)	-	-	104	809	148
Air Pollution Control Costs ($000)					
Particulates	-	-	-	410	287
SO_2 control	-	-	2,425	4,535	-
HCl control	-	-	114	220	-
Fluoride	7,040 *	7,740 *	-	-	7,040 *
TOTAL	7,040 *	7,740 *	2,643	5,974	7,475 *
Unit cost, $/ton Al	44	37.20	16.50	37.35	46.72

Source: Arthur D. Little, Inc. estimates

*Includes air, water, and solids pollution control.

TABLE IV-16

ENERGY CONSUMPTION SUMMARY FOR ENVIRONMENTAL CONTROL IN ALUMINUM INDUSTRY

Base Line: Hall-Heroult Cells for Aluminum
Bayer Process for Alumina

	Base line	Alternative Processes		Combination Processes	
	Hall	Existing Hall with TiB_2 cathodes	New ALCOA Chloride	Toth Clay-ALCOA Chloride	Bayer-Hall/Heroult
Production basis, ton/yr	160,000	208,000	160,000	160,000	160,000
Water Pollution Control					
Electric power (10^6 kWh/yr)	- *	- *	0.054	0.075	0.02
Air Pollution Control					
Electric power (10^6 kWh/yr)	26	26	6.35	14.93	27.6
Total Electric Power (10^6 kWh/yr)	26	26	6.40	15.01	27.62
Total Fuel Equivalent (10^6 Btu/yr)**	273,000	273,000	67,200	157,600	290,000
Unit Energy Consumption (10^6 Btu/ton Al)	1.71	1.31	0.42	0.99	1.81

*Included in Air Pollution Control.

**@ 10,500 Btu/kWh.

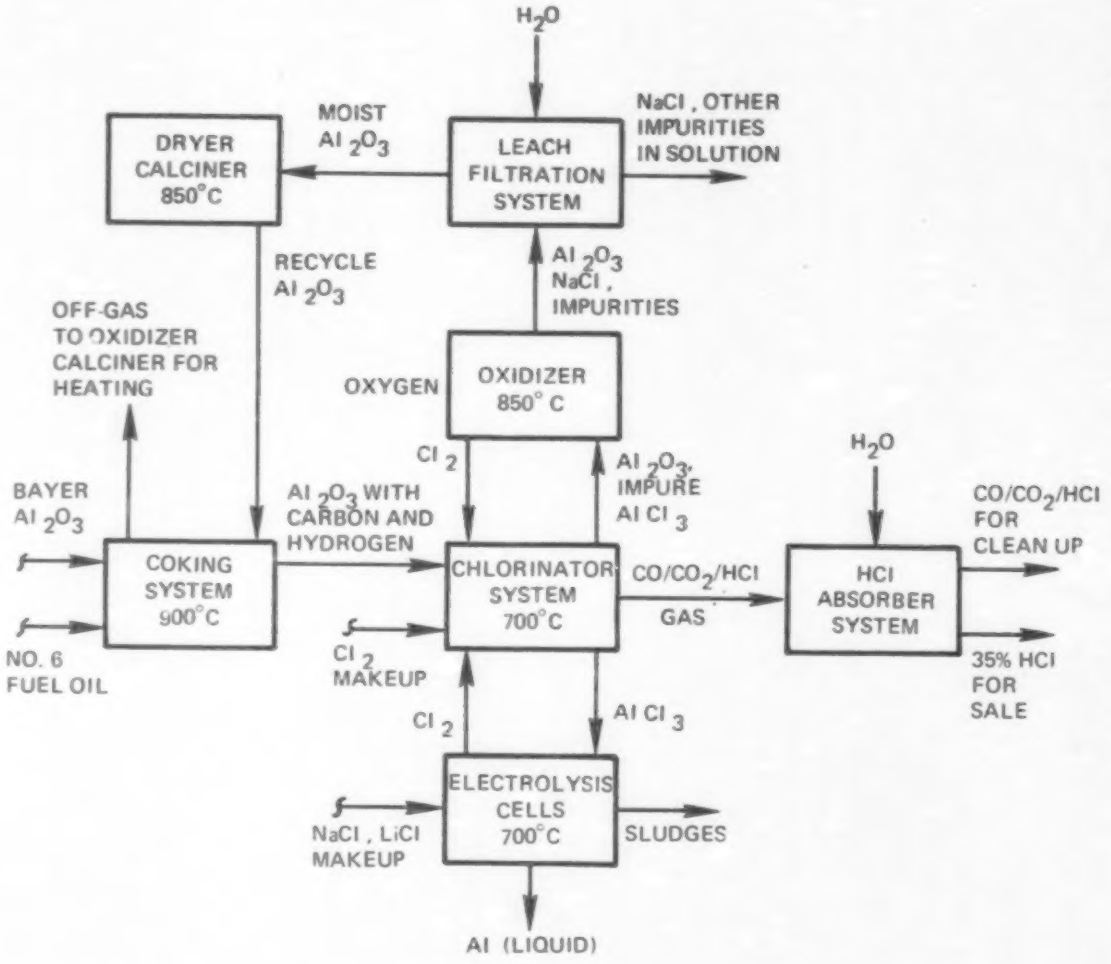

H2O
DRYER CALCINER 850°C
MOIST Al2O3
LEACH FILTRATION SYSTEM
NaCl, OTHER IMPURITIES IN SOLUTION
RECYCLE Al2O3
Al2O3 NaCl, IMPURITIES
OFF-GAS TO OXIDIZER CALCINER FOR HEATING
OXYGEN
OXIDIZER 850° C
Cl2
Al2O3, IMPURE AlCl3
H2O
BAYER Al2O3
Al2O3 WITH CARBON AND HYDROGEN
CO/CO2/HCl FOR CLEAN UP
COKING SYSTEM 900°C
CHLORINATOR SYSTEM 700°C
CO/CO2/HCl GAS
HCl ABSORBER SYSTEM
NO. 6 FUEL OIL
Cl2 MAKEUP
35% HCl FOR SALE
Cl2
AlCl3
NaCl, LiCl MAKEUP
ELECTROLYSIS CELLS 700°C
SLUDGES
Al (LIQUID)

Figure IV-4. Alcoa Chloride Process (Assumed Scheme)

the fuel oil is deposited on the alumina. This bottom bed is equipped with heating fingers or tubes in which a portion of the cracked off-gas is burned with the air to provide heat for coking and deposition of carbon on the alumina. The off-gases from this combustion could contain sulfur (SO_2) which would have to be removed by scrubbing. Feed rates are such as to deposit on the alumina a slight excess of carbon over the stoichiometric amount required to remove the oxygen in the alumina and yield a mixture of primarily carbon dioxide with some carbon monoxide in the subsequent chlorination step.

(2) Chlorination

The alumina, with a slight excess of carbon over the stoichiometric for removal of combined oxygen as carbon dioxide, then goes to the chlorination system. Chlorination is carried out in a fluid-bed system operated at about 1,300°F in which the alumina is converted to volatile aluminum chloride in non-condensable off-gases, primarily carbon dioxide and carbon monoxide (70-30 volume ratio). The off-gases from the chlorination also contain some hydrogen chloride from the reaction of chlorine with the hydrogen adsorbed on the coked alumina feed. The off-gases also contain sodium chloride vapor in an amount equal to most of the sodium present in the alumina feed and perhaps some highly volatile sulfur chlorides and some vanadium tetrachloride as well, introduced into the system with the oil. However, we believe that a vanadium-containing oil could not be tolerated in this process because tetrachloride would form and condense with the aluminum chloride, subsequently contaminating the metal.

(3) Off-Gas Handling and Impurities Removal

The off-gases, primarily aluminum chloride, are then subjected to high-temperature condensation which takes out sodium chloride, some aluminum chloride, and unreacted alumina. This condensate is separated and then oxidized to recover chlorine for recycle by oxidation of the aluminum chloride to alumina. The resulting solid mass is then subjected to a water leach filtration circuit to remove the soluble sodium chloride and recover alumina for recycle. The leached salt solution would be a source of water pollution that would have to be impounded. The recovered alumina is dried and calcined at 1,560°F, and then recycled to the fluid-bed coking system described above. The major portion of aluminum chloride is not condensed and passes through the high-temperature condensation along with the gases that consist largely of carbon monoxide, carbon dioxide, and hydrogen chloride. This gas is then subjected to a final condensation at about 150°F to remove, as solid or liquid, aluminum chloride which is the product feed to the electrolytic cells. The remaining noncondensable gases--carbon monoxide, carbon dioxide and hydrogen chloride--then pass to an absorption system in which the hydrogen chloride is absorbed to produce a byproduct 35% hydrochloric acid solution which is available for sale. The off-gases from this scrubber would be burned, probably in a carbon monoxide boiler, or flared.

(4) Cell Operations

Cell electrolyte consists of 5% aluminum chloride and a mixture of sodium chloride and lithium chloride. Both the cathode and anode are inert carbon electrodes, i.e., non-consumable electrodes. Since they are inert, it is unlikely that either the anode or the cathode would be produced at the aluminum smelter, but rather that they both would be purchased from the suppliers of carbon electrodes.

Sodium aluminate tends to build up as sludge in the cell system. This sludge must be removed periodically from the cell and, when removed, tends to carry with it some electrolyte containing sodium chloride, lithium chloride, and aluminum chloride. Thus there is a requirement for lithium and sodium chloride make-up. The cells would be completely covered to recover the byproduct chlorine from the anode and any aluminum chloride vapor from the cell electrolyte. However, aluminum chloride vapor losses are expected to be very small, because the vapor pressure of aluminum chloride is reduced to a very low level as a result of the formation of a double salt with sodium chloride which has a low-vapor pressure.

The cell operates at about 1,290°F, much lower than the 1,770°F average for the Hall cells. It is likely that the cells would operate at slight positive pressure to avoid air or water in-leakage which would be detrimental to their operation by forming oxide sludge on the cathode; this would reduce the current efficiency. It is likely that there would be some fugitive emissions from these cells that are likely to be operated at slight positive pressure. It is almost impossible to feed a solid, such as aluminum chloride, and electrolyte make-up sodium and lithium chloride, or remove sludge from a closed system under slight positive pressure without some fugitive gaseous emissions. Some provisions would have to be made to ventilate the cell room to remove chlorine and aluminum chloride, if present, by scrubbing the gas collected through roof monitors.

The make-up requirements to the process are chlorine, sodium chloride, and lithium chloride. Make-up chlorine is required because any hydrogen or water entering the chlorinator forms HCl, which exits with off-gases and is absorbed to produce an impure muriatic acid for sale as a byproduct. Sodium and lithium chloride make-up is required to make up for losses or electrolyte removed as sludge--largely sodium aluminate from the cell.

The advantages of the Alcoa chloride electrolysis relative to the existing Hall oxide electrolysis appear to be the following:

- The electrical energy requirement is sharply reduced, because the decomposition voltage and the bath resistivity are both lower for the chloride melt;

- By eliminating oxygen from the system, the chloride process does away with the need to continually fabricate and replace the consumable carbon anodes; instead, permanent graphite electrodes can be used, and the expensive energy-consuming anode baking facilities eliminated;

- Because electrodes can now be permanently emplaced, it is possible to design chloride process cells with multiple sheet electrodes stacked one above another (the so-called "multipolar" electrode configuration) so that one cell then becomes the equivalent of several single-cells, with consequent savings afforded by the much more compact cell design;

- The chloride cell operating temperature is about 1292°F rather than than the 1742°-1832°F temperature of the Hall process;

- The fluoride emissions of the Hall process are completely avoided since no cryolite or fluoride materials are used in the chloride process.

(5) Pollution Control

Water Pollution Considerations

Since alumina is the basic raw material for both the Hall process and the Alcoa chloride process, those waterborne pollutants (heavy metals) emanating directly from the alumina itself will be substantially the same for both processes. It is reasonable to expect that, as in the case of the existing process, plants using the Alcoa chloride process will not have to comply with specific limitations on heavy metals.

Unlike the Hall process, the Alcoa chloride process does not use a fluoride-containing fluxing agent, eliminates the fluxing agent, and consequently eliminates the fluoride emissions. This feature represents a definite advantage over the existing process in terms of water pollution control.

The Alcoa chloride process does, however, produce a chloride-containing wastewater stream. In this process the bulk of the chlorine stream used in the process is recycled. A small fraction of the chlorine is unavoidably lost from the chlorine recycle loop and eventually enters the total wastewater stream as chloride. A small amount of sodium ion (also inherent in the existing process) also comes in contact with water. Thus, the wastewater from the Alcoa chloride process contains a quantity of sodium and chloride that is not present in the wastewater from the existing process.

To assess the significance of the previously non-existent sodium chloride wastewater load, data from the NPDES discharge permit of the Alcoa demonstration plant in Palestine, Texas were examined, in conjunction with calculated quantities of sodium chloride, and then extrapolated up to the base case 160,000-ton/yr aluminum plant. The following is our estimate of the sodium chloride pollutional load for a 160,000-ton/yr plant.

- Wastewater flow rate = 1,230,000 gal/day;

- Total sodium chloride wasteload = 12,300 lb/day;

- Sodium chloride concentration = 1,200 mg/l.

The above estimate represents the maximum quantity of sodium chloride anticipated, as a definite fraction of sodium will leave the plant in the aluminum itself and be entrapped in the solid sludges removed from the cells. The quantity and concentration of the sodium chloride permits discharge to receiving waters under the present effluent limitation guidelines. However, water quality limitations for some locations may result in restrictions. For purposes of estimating wastewater pollution control costs, it has been assumed that discharge to surface waters would be permitted.

During the chlorination part of the process, alumina, carbon (from cracked No. 6 fuel oil), and chlorine are contacted in a fluidized state. It is possible that chlorine could react with certain residual hydrocarbon compounds to form chlorinated hydrocarbons, a potential pollutant. If indeed this phenomenon does occur and is found to be a serious problem, one possible solution is the installation of a combustion chamber to incinerate the chlorinated hydrocarbons.

It is, however, quite possible that the Alcoa chloride process will actually produce less waterborne organic pollutants than the existing process, due to the elimination of the anode baking plants, since it employs non-consumable graphite anodes. However, the Alcoa chloride process uses large volumes of process cooling water. If the cooling water is recirculated through a cooling tower, as is the conventional practice where large flow rates are included, a small purge stream or blowdown will be discharged, as a wastewater effluent. In such cooling water circuits, chromate corrosion inhibitors are often added and will, therefore, be present in the cooling tower blowdown. If appreciable amounts of chromates are used, the cooling tower blowdown will have to be subjected to chromium removal prior to discharge.

Chromium removal involves two steps, reduction and precipitation. It is necessary to first reduce chromium in the hexavalent form to the less toxic and more easily removed trivalent form. The soluble chromium is then precipitated from solution and separated from the liquid stream. Typically, sulfur dioxide is used as the reducing agent and lime is used for the precipitation step.

The 160,000-ton/yr plant has a cooling water circulation rate of 53,000,000 gal/day. With a blowdown rate of 2%, the cooling tower blowdown flow rate would be 1,060,000 gal/day. While the chromium concentration of the blowdown can vary considerably, 30 mg/l would be a typical concentration. By employing the above treatment process, chromium concentrations of less than 0.1 mg/l could be achieved. Cost estimates for such a chromium treatment system are presented in Table IV-17.

Air Pollution Considerations

Because of the hazards of working with chlorine, the gas systems would of necessity be quite tight. After solids recovery, there are two potential emission sources which would require treatment:

- The exhaust from coke-making (if manufactured rather than purchased); and
- The exhaust from the HCl absorption system.

Theoretically, the process can work using a variety of fuels--purchased coke, coal, oil, or even natural gas--but we believe that the method described in the patents, using oil as described above, is the preferred method. Thus, we have chosen an example based on No. 6 fuel oil with a 1% sulfur content.

TABLE IV-17

ALCOA CHLORIDE PROCESS COOLING TOWER BLOWDOWN WASTEWATER TREATMENT COSTS
(Basis: 160,000 Ton/Yr Aluminum Production)

CAPITAL INVESTMENT - $375,000

	Annual Quantity	Cost per Unit Quantity	Quantity per Ton of Production	$ per Ton of Product
VARIABLE COSTS				
Operating Labor (including suprvis + OHD)	1,800 man-hr/yr	$11.38/man-hr	0.0113	0.1281
Maintenance (Including Labor + OHD)	-	-	-	0.0938
Chemicals				
• Sulfur Dioxide	75 ton/yr	$340/ton	4.7×10^{-4}	0.1594
• Lime	80 ton/yr	$30.75/ton	5.0×10^{-4}	0.0156
• Sulfuric Acid	38 ton/yr	$51.15/ton	2.4×10^{-4}	0.0119
Fuel	-	-	-	-
Electrical Power	53,700 kWh/yr	0.012/kWh	0.34	0.0038
Sludge Disposal	750 ton/yr (@ 10% solids)	$5.00/ton	4.7×10^{-3}	0.0238
TOTAL VARIABLE COST				0.4364
FIXED COST				
Taxes & Insurance (@ 2%)	-	-	-	0.0469
Depreciation (@ 7.1%)	-	-	-	0.1664
TOTAL FIXED COST				0.2133
TOTAL ANNUAL COST				0.6497
RETURN ON INVESTMENT @ 20%				0.4688
TOTAL				1.1185

Notes: 1. Treatment costs are based on a cooling tower blowdown flow rate of 1.0 10[illegible] gal/day (2% blowdown) and a chromium concentration of 30 mg/l.

2. Treatment consists of reduction followed by lime precipitation and clarification.

This means that the burned off-gases from the coker must be treated to remove sulfur emissions. Because of the extremely high sulfur loadings expected, the stack scrubbing process used should be regenerative. Most of the scrubbing processes appropriate for this type of control were developed for utility boilers. Such systems include a scrubbing system (for gas-liquid contact) and an alkali handling system (for regeneration of caustic, for example). These systems have been proven effective on pilot-scale systems, and several full-scale systems are now in operation.

The other waste gas stream which requires control is the exhaust from the HCl absorption system. The exhaust contains primary CO, CO_2, minor amounts of HCl and perhaps traces of Cl_2. Control of this exhaust is not nearly as complicated or expensive as the control of sulfur. A caustic scrubbing system using a venturi or spray tower is all that is required. The discharged scrubber water contains inorganic salts and, under present guideline limitations, could be discharged with the treated wastewater stream. Table IV-18 summarizes our estimates for SO_2 and HCl pollution control costs.

Solid Waste

Various sludges removed from the electrolyte at times would amount to about 0.005 ton per ton of aluminum; the sludge would be predominantly sodium aluminate contaminated with NaCl/LiCl. Purges of unchlorinatable Al_2O_3 from the chlorinator might amount to 0.03 ton per ton of aluminum.

TABLE IV-18

SO_2 AND HCl POLLUTION CONTROL COSTS FOR ALCOA CHLORIDE PROCESS (Basis: 160,000-Ton/Yr Aluminum Production)

	Units Used in Costing or Annual Cost Basis	$/Unit	SO_2 Control	HCl Control
CAPITAL INVESTMENT (CI)			$3,700,000	$155,000
VARIABLE COSTS				
Electric Power Purchased	kWh	0.012	75,000	1,200
Labor Wages	man-hr	$6.50	57,000	1,000
Supervisory Wages	15% labor		8,600	150
Maintenance Labor, Supervision, Materials and Supplies	5% CI		185,000	7,750
Labor Overhead	32% wages		21,000	370
Chemicals				
• Lime	ton	30.75	759,800	-
• Soda Ash	ton	56.00	-	57,400
Residue Disposal	ton	5.00	200,500	-
Total			1,306,900	67,870
FIXED COSTS				
Plant Overhead	60% wages		39,400	690
Local Taxes and Insurance	2% CI		74,000	3,100
Depreciation	CI/14		264,300	11,000
TOTAL PRODUCTION COSTS			1,684,600	2,660
Return on Investment (pretax)	20% CI		740,000	31,000
TOTAL ($/yr)			2,424,600	113,660
TOTAL ($ per ton aluminum)			$15.15	$0.71

Every four years or so when the cells are relined, the old refractory would have to be discarded. Similarly there would be miscellaneous minor wastes from the aluminum casting operations; much of these latter wastes would, in any case, be similar to those from the Hall process. The properties of these solid wastes should permit disposal to approved chemical landfills.

Pollution Control Costs and Energy Use

Tables IV-14, IV-15 and IV-16 summarize pollution control costs and energy use for the Alcoa process. The major user of energy for environmental control is the scrubber for the SO_2 system. Both costs and energy use for pollution control are estimated to be considerably less than the base line Hall process where pollution control energy use amounts to less than 1% of total process requirements.

(6) Process Energy Use

One of the chief advantages claimed for the chloride process relative to the Hall process is its lower electrical requirement, about 5.2 kWh/lb of aluminum, delivered at a potential of 3.3 volts (U.S. Patent 3,725,222). For a bath of about 5% $AlCl_3$ in 50% NaCl/LiCl, the reversible decomposition voltage is about 1.95 volt (U.S. Patent 3,847,761). The current efficiency, using 12,158 ampere-hours per lb-equivalent as the value of the Faraday and remembering that there are three equivalents per lb mol (27 lb) of aluminum, is easily shown to be quite high:

$$\text{Current Efficiency} = \frac{3 \times 12{,}158}{(5.2 \times 1{,}000/3.3)\ \ (27)} = 86\%$$

Note that the chloride process figure of 5.2 kWh/lb aluminum compares very favorably with the 7.8 and 6 kWh/lb aluminum needed for the present and projected new Hall-Heroult cells respectively.

The fossil fuel requirement of about 25×10^6 Btu/ton of aluminum in the chloride process is higher than that of the Hall process; when one considers the fuel value of the coke, pitch, and natural gas in the Hall process, the total fuel value of "fossil-based materials" is about the same for the two processes. The Alcoa chloride process energy savings are largely due to the smaller electrical power utilization.

(7) Economic Factors

It is difficult to estimate costs for this process, for which details are lacking. It has been suggested (Peacey and Davenport, July 1974) that a new chloride plant ought to be somewhat cheaper than a new Hall plant. We believe these authors have not adequately taken into account the complexity of the chloride process, which counteracts the savings from elimination of the anode-baking operation and from the smaller floor area for the multipolar cells. On this basis, we have chosen to equate the capital investment for both processes at $1,750/annual ton of aluminum (March 1975 basis).

An estimate of the operating cost for a new Alcoa chloride process plant is shown in Table IV-19. Table IV-19 presents the cost of the operation described above which we believe is the preferred method of operating this process. As seen, the estimated cost for environmental control for the Alcoa process is only a small fraction of the production costs.

(8) Technical Considerations

The degree of technical risk is not known, but Alcoa presumably would not be building a 15,000-ton/yr demonstration smelter unless it were optimistic about the process. There is a good body of information on reductive chlorination of ores and on separation of volatile metal chlorides; molten salt chloride electrolysis is already commercial practice in the manufacture of magnesium metal. For these reasons, we believe that the risk of technical failure is not a major one for the Alcoa chloride process. There may, on the other hand, be problems with impurity buildups in portions of the processing loop, or in lower chlorination yields than expected, etc., which can affect the projected costs. Such problems ought to be soluble, however, and the process appears ultimately to offer some significant advantages over the Hall process.

b. Refractory Hard Metal Cathodes

(1) Background

The prospect of refractory hard metal cathodes for use in the aluminum industry has been of interest for some 15-18 years. Early work on this subject

TABLE IV-19

ESTIMATED PRODUCTION COSTS FOR NEW ALUMINUM PLANT, 1975
(Alcoa Chloride Process)

Product: Aluminum
Process: Alcoa Chloride
Location: Kentucky-Tennessee
Annual Capacity: 160,000 tons
Capital Investment: $280,000,000
Annual Production: 160,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
• Bayer Alumina	ton	125.00	1.93	241.25
• Oxygen	ton	25.00	0.02	0.40
• NaCl	ton	30.00	0.001	0.03
• LiCl	ton	2000.00	0.001	2.00
• Chlorine	ton	105.00	0.19	19.95
Byproduct Credits				
• 35% HCl Solution	ton HCL	27.00	-0.19	-5.08
Energy				
• Purchased Fuel (No. 6 Fuel Oil)	10^6 Btu	2.00	24.85	49.70
• Electric Power Purchased	kWh	0.012	10500.00	126.00
• Miscellaneous				
Water				
• Process	10^3 gal	0.50	0.2	0.10
• Cooling	10^3 gal	0.05	100.00	5.00
Direct Operating Labor (Wages)	Man-hr	6.50	3.5	22.75
Direct Supervisory Wages	15% Op. Lbr.			3.41
Maintenance Labor (Wages)	Man-hr	6.50	4.5	29.25
Maintenance Supervision (Wages)	15% Mnt. Lbr.			4.38
Maintenance Materials	2.5% CI			43.75
Labor Overhead	32% of wages			19.13
Misc. Variable Costs/Credits				
TOTAL VARIABLE COSTS				562.02
FIXED COST				
Plant Overhead	60% of wages			35.87
Local Taxes and Insurance	2% of CI			35.00
Depreciation	7.1% of CI			124.25
TOTAL PRODUCTION COSTS				757.14
Return on Investment (pretax)	20% of CI			350.00
Pollution Control				16.50
TOTAL				1,123.64

was carried out by Kaiser and British Aluminum. In the early days, several different materials were considered as potential refractory hard metals for use as cathodes in place of the graphite cathodes presently used in the Hall-Heroult cells. The materials originally considered were zirconium and titanium carbides and borides and some mixtures thereof.

Since then, carbides of both metals and zirconium boride have been eliminated from consideration so that, at present, principal interest is in titanium diboride because of its superior electrical conductivity, and the fact that it is wetted by molten aluminum and cryolite in the cell. Also, in the pure state it is not corroded by the electrolyte. Thus, there is hope that this material, properly fabricated, would last for a minimum of four years. This is the requirement for cathodes since the cell itself has a normal life of four years, although some cell lives have been reported to last up to six years.

(2) Past Difficulties and Considerations

Originally, these materials were considered as a means of reducing the voltage drop at the various interfaces in the cathode hardware. In the present cathode arrangement used in the Hall cells, there are four connections, each of which involves a certain amount of voltage drop. The first connection is the one between the bus bar and the iron cathode support--current distribution bar; the second, between the iron and the carbon cathode; the third, between the carbon cathode and the molten aluminum; and the fourth, between the molten aluminum and the electrolyte. Of these, the most important, i.e., the one having the highest voltage drop, occurs between the carbon and the molten aluminum metal pad which results partly from the formation of sludge and aluminum carbide at this interface. Under the best conditions, the drop across this interface is 0.4 volt, but it can be as high as 0.75 volt. The voltage drop between the cathode bus to the surface of the carbon anode amounts to a total of about 0.5 volt.

Originally, the thinking was to eliminate the voltage drop between the iron and the carbon and to reduce the voltage drop between the cathode bus and the aluminum pad by replacing the iron and carbon with titanium diboride. In theory, it can be shown quite readily that the voltage drop incurred in passing electric current through a conductor of optimum dimensions and with a normal Lorenz function with respect to thermal and electrical conductivity when the ends are maintained (as in aluminum cells) at 95°F and 1785°F is on the order of 0.18-0.19 volt. This means that if an appropriate material, such as titanium diboride, could be produced, the cathode voltage drop might be reduced to less than half of the existing value.

This concept would remove the iron and carbon from the cathode system to be replaced by titanium diboride, which is much more compatible with molten aluminum than the carbon presently used, because high-resistance aluminum carbide forms at this interface. This, in turn, creates more heat in the cathode as a source of power loss to heat rather than disassociation of aluminum oxide in the electrolyte. However, by replacing the iron and carbon of the cathode with titanium diboride, the savings in power would amount to only 5-10%.

The important reason that nothing has been done with this concept in the past is that there have been difficulties with the stability of the titanium diboride cathodes due to spalling, cracking, and, in general, short cathode life in the cell. Part of these past difficulties may have been due to the presence of titanium carbide as an impurity from the original manufacturing process for producing titanium diboride. It is now well known that titanium carbide makes the titanium diboride more sensitive to corrosion, stress cracking, and thermal shock.

(3) Present Concepts and Activities

More recently, interest has shifted to replacing not only the iron and the carbon, but also the molten aluminum pad so that the titanium diboride would provide connections between the cathode bus and the electrolyte. There is a much greater advantage in this arrangement because it implies that the aluminum produced at the cathode could be rapidly removed or drained from the cathode so that only a thin film of molten aluminum would ever exist on the titanium diboride. This would significantly reduce the drop through the molten aluminum. It has further advantages in the cell system. Because there would be only a thin film of molten aluminum on the cathode, which would reduce or largely eliminate the back reaction that occurs at the anode, aluminum reacting with CO_2 to form CO and aluminum oxide would be minimized and the Faraday efficiency improved. In conventional Hall-Heroult cells, the high current flux tends to create a so-called fog of aluminum particles between the anode and cathode in the electrolyte, which provides opportunity for this back reaction. With thin films of molten aluminum on the titanium diboride cathodes, there is little, if any, tendency to sweep molten aluminum from the titanium diboride surface wetted by the molten aluminum. This would permit closing the distance between the anode and cathode which, in turns, would reduce the voltage drop through the electrolyte, and at the same time permit an increase in anode current density. This in turn would mean more current flow and more disassociation so that more aluminum would be produced.

It is anticipated by those working on this development in the industry that a power saving of the order of 30-40% could be achieved during periods of production curtailment, i.e., periods of low aluminum demand. In addition, it is also believed that during periods of high demand, current flow could be increased and, therefore, production would be increased. This would require reducing the anode/cathode distance to reduce the voltage drop and avoid overheating the cell by the higher current flow. It is currently believed that production increases with corresponding current flow increases of 30-50% are possible. It is unlikely that any power saving would result from a 50% increase in current flow and 50% increase in production. However, it is conservatively believed that a 15-20% saving in power, along with a simultaneous 30% increase in production, is attainable. This contention is based upon some current experience and expectation that satisfactory titanium diboride cathodes can be made that will survive the atmosphere of the electrolyte in the Hall-Heroult cells for four to five years. Apparently, at least two companies, specifically Kawecki Berylco Industries, Inc. and PPG Industries, feel that the past difficulties with titanium diboride have now been overcome, and they believe that they could demonstrate long (3-4 years) cathode life and the advantages of titanium diboride cathodes to the aluminum companies.

In the past, and even now, the aluminum companies have looked to producers of these refractory hard metals to provide materials that would operate satisfactorily in the aluminum cells. The aluminum companies have been cooperative in terms of testing and analyzing the results, but have not undertaken much internal research on the problem of providing the desired cathode materials. The remaining problems seem to be a full demonstration of cathode life, which must be at least four years, and hopefully, longer. Views differ in the industry with respect to the present situation. Some believe that the price of the fabricated materials is too high, which is the view of British Aluminum, while others believe that the potential saving would support a very high price for the new titanium boride cathodes.

(4) Costs of the Cathodes

It is difficult to obtain real costs or prices for titanium diboride cathodes that will ultimately apply, because each of the aluminum producers has different conceptual configurations which they consider to be proprietary. Moreover, although these configurations are known to suppliers, they are privileged information which cannot be released. However, we understand that the raw material cost is \$15.50-\$22.00/lb and that fabrication is presently 2.5 times that number, which means that a cubic inch of fabricated titanium diboride would cost about \$38.75. It must be recognized that at present there is no large-scale production or fabrication of these materials and that the cost would logically be much higher now than in the future. If this development becomes a commercial reality in the aluminum industry, production volume would increase and costs for fabricated cathodes might be one-half to one-third of these present costs. Conventional carbon cathodes that last 3-4 years would cost \$2-3 per ton of aluminum produced over the above life of the cell.

There is no doubt that the cost of fabricated diboride would be much higher than present carbon cathodes. Therefore, the titanium diboride cathode configurations must have a high surface-to-weight ratio. This probably means thin sections which may require supports. Among the aluminum producers that are active in this field, there is a lot of work going on with respect to titanium diboride cathode configurations and the support of such thin sections in the cell.

(5) Status of Development

There is at present an increased activity and excitement in the aluminum industry and among producers of titanium diboride with respect to the potential of cathodes made from this material in the reduction cells. The problem is to demonstrate life under active cell operations and, if a four-year life is demonstrated, we believe that rapid implementation can be expected. The incentives are so great that increased activity on this development is expected. In view of the above, it is difficult to set a time expectation on implementation.

(6) Effluent Control

As discussed in Appendix C, which deals with the pollution problems of the existing Hall primary aluminum smelting process, the major sources of water pollution are wastewater streams created by the use of wet air pollution control devices. Major pollutants of concern from existing aluminum smelting operations are fluorides and suspended solids.

Although a number of the heavy metals present as impurities in the alumina feed may ultimately find their way into wastewater streams, these usually occur in such low concentrations as to make their removal either technically or economically impracticable, a fact recognized in the establishment of guidelines for the 1973 and 1983 effluent limitations. Since the effluent limitations are applied only to suspended solids, fluoride, and pH, it is important to recognize what effects the retrofitting of present smelters with titanium diboride cathode might have on the capabilities of presently installed pollution control equipment in meeting effluent limitation guidelines.

The existing Hall process uses cryolite and aluminum fluoride as fluxing agents, thereby producing an off-gas consisting largely of equal parts of carbon dioxide and carbon monoxide, particulates in the form of insoluble fluorides, hydrogen fluoride and fluorine. The effect of the use of titanium diboride cathode in the Hall-Heroult cells would be as follows:

- The back reaction in which aluminum reacts with carbon dioxide to produce alumina and carbon monoxide would be substantially reduced; this would mean that the off-gas would contain less carbon monoxide and more carbon dioxide. It would also mean that a slightly lower, or the same, volume of carbonaceous gas would be released at the anode, even assuming that the production rate would increase per cell by 30%.

- Fluoride and particulate emissions are related to aluminum production so that the concentration of fluorides in the off-gases from the cell would increase by approximately 30% as a result of the increased production possible.

Thus, as suggested by the estimated pollution control costs shown in Table IV-14, we judge that the overall effect would be about the same volume of off-gas per unit time with a 30% increase in the fluoride and particulate content of the gas. Consequently, in a retrofit situation it is likely that off-gas handling equipment would be generally adequate in most existing smelters to handle the off-gases resulting from the installation of titanium diboride cathodes. However, capacity would have to be checked in each retrofit. On the other hand, the feed rate of any reagents, such as calcium oxide or alumina used to eliminate fluorides--calcium fluoride, cryolite, or aluminum fluoride--would have to be increased to take care of the increased emissions of fluorides from the cells as a result of increased production. The increases would be proportional to the increase in aluminum production rate.

Obviously, if the dry emission control process were installed on an existing smelter, the effect, even on a fluoride recovery system, would be minor because, while more fluoride would be emitted per unit time, more alumina would be consumed and would be available for removing fluorides as aluminum fluoride, which would go back as feed to the cell, i.e., the rates would be proportional.

The net result is that we doubt that there would be any significant effect on pollution control systems presently existing in aluminum smelters as a result of retrofitting the installations with titanium diboride cathodes in place of the graphite cathodes presently used. It should be understood that in either case--carbon or titanium diboride--the cathode is inert, i.e., it does not enter into the reaction, only the anode carbon is consumed and, of course, is the source of the carbon monoxide and carbon dioxide emitting from the existing cells. The same would still be true after the installation of titanium diboride cathodes.

With regard to the solid waste problem inherent in the disposal of old refractory linings removed before rebuilding cells, this problem would also remain unchanged if we assume the same cell life. This would have to be the case, because the titanium diboride cathode would not be installed if its use significantly reduced cell life. The value of the titanium diboride scrap cathode is high enough to recover the material for return to the cathode manufacturers.

(7) Energy Use

If the back reaction, which presently occurs in the anode of the conventional Hall-Heroult cell operation, is largely eliminated, as might be expected with the use of titanium diboride cathodes, then there would be a reduction in the consumption of anode carbon - and therefore, petroleum coke and pitch - of about 20%. This means there would be a reduction in purchased fuel from 24 x 10^6 Btu consumed per ton of aluminum by the present smelters to about 20 x 10^6 Btu/ton of aluminum when titanium diboride cathodes were used. Power consumption would be reduced from 15,600 kWh/ton in existing smelters to 12,480 kWh/ton of aluminum. Converted to a fossil fuel equivalent basis, i.e., considering the inefficiencies in power generation, the total energy consumption amounts to 151.2 x 10^6 Btu with the use of titanium diboride cathodes. This compares favorably with the total energy consumption in the existing smelting process using carbon cathodes, which is 187.8 x 10^6 Btu/ton of aluminum. As with the base line Hall process, pollution control energy use is less than 1% of process energy requirements. Thus an overall energy saving of 19% is potentially achievable by conversion to titanium diboride cathodes.

(8) Economic Factors

It is difficult to anticipate how the industry will take advantage of this development. We have assumed it will retrofit its existing large cells to take advantage of the potential of increasing production, while at the same time reducing energy consumption by 20%, as appears possible with the use of titanium diboride cathodes. This approach would permit retiring some of the older, less efficient pot lines that have relatively small cells by today's standards. Of course, the major consideration is electrical power so that it is unlikely the industry would retire cell lines in areas where there is a continued potential for low-cost power. Nevertheless, we doubt that they would use the total potential for energy savings, except in periods of production curtailment. In Table IV-20 we have presented our estimates of the costs resulting from the application of titanium diboride cathodes in an existing carbon cathode smelter of 160,000-ton/yr nominal capacity; such a change would increase smelter output by 30% to an estimated 208,000-ton/yr and would have further cost consequences as discussed below.

If the back reaction could be entirely eliminated at the anode, the anode consumption could be reduced by 25%. However, we have assumed that the back reaction would be largely, but not entirely, eliminated, so that calcined coke and pitch consumption would be reduced by only 20%.

As mentioned above, we also assumed that the power consumption would be reduced by 20%, while the cell lines would be producing approximately 30% more metal. There would be a slight reduction in operating labor and operating labor supervision, but no reduction in maintenance labor and maintenance supervision. We have included an estimated cost for titanium diboride cathodes. This is actually an amortization factor assuming a four-year cathode life at a cost of $12.90/cu in.

This calculation is based on several assumptions. First, we assumed that the costs of titanium diboride cathodes, fully fabricated, would be reduced to one-third of present costs, based upon the assumption that, with large-scale production and fabrication of cathodes, costs would be reduced to this extent, and that costs would be substantial but affordable, as one of the men working in the field said. We also assumed that the cathodes would be fabricated in tiles or sheets 3/16 in. in thickness supported by suitable refractory or carbon blocks. This is based on our understanding that the fabrication would be in relatively thin sections with a high surface-to-weight or -volume ratio to minimize the cost of titanium diboride cathodes per unit area. We further assumed that the current density would be increased by about 30% of that presently used in carbon cathodes.

The costs presented in Table IV-20 for an older aluminum smelter with a nominal capacity of 160,000-ton/yr producing 208,000-ton/yr with titanium diboride cells would typically have an undepreciated investment of about $140 million. This is about average for the present existing aluminum industry, based on information obtained from major financing sources. This basis includes the additional investment would have to be made, amounting to $42 million, to provide some increase in capacity for handling the increased production of aluminum, increased storage and handling for alumina, cryolite, aluminum fluoride, and increased capacity for pollution control.

An existing plant retrofitted with titanium diboride cathodes would produce aluminum at $733/ton. This is about the same as for a plant operating conventionally with carbon cathodes, which would produce aluminum at a cost of $742/ton. Although this seems like a minor reduction, it becomes a much

TABLE IV-20

ESTIMATED PRODUCTION COSTS IN EXISTING ALUMINUM PLANT WITH TITANIUM DIBORIDE CATHODES, 1975

Product: Aluminum
Process: Hall with Titanium Diboride Cathodes
Location: Kentucky-Tennessee
Annual Capacity: 208,000 Net Tons
Fixed Investment: *
Annual Production: 208,000 Net Tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
● Bayer Alumina	net ton	125.00	1.93	241.25
● Cryolite	net ton	336.00	0.035	11.76
● Aluminum Fluoride	net ton	350.00	0.020	7.00
Energy				
● Purchased Fuel				
Natural Gas	10^6 Btu	1.50	6.1	9.90
● Calcined Coke	net ton	80.00	0.42	33.60
● Pitch	net ton	70.60	0.12	8.47
● Electric Power Purchased	kWh	0.01	12,480.00	124.80
● Miscellaneous				
Water				
● Process				
● Cooling				
Direct Operating Labor (Wages)	Man-hr	6.50	2.5	16.25
Direct Supervisory Wages	15% of Op. Lbr.			2.44
Maintenance Labor (Wages)	Man-hr	6.50	4.5	29.25
Maintenance Supervision (Wages)	15% of Mnt. Lbr.			4.39
Maintenance Materials	2.5% of RC			38.70
Labor Overhead	32% of wages			16.74
Misc. Variable Costs/Credits				
● Cost Titanium Diboride Cathodes	Est.			25.73
TOTAL VARIABLE COSTS				569.55
FIXED COSTS				
Plant Overhead	60% of wages			31.39
Local Taxes and Insurance	2% of UI			13.46
Depreciation	7.1% of UI			47.79
TOTAL PRODUCTION COSTS				662.19
Return on Investment (pretax)	5% of UI			33.65
Pollution Control				37.20
TOTAL				733.04

*Undepreciated Investment (U.I.) $140,000,000
1975 Replacement Costs $280,000,000 +
New Investment for Retrofitting (R.C.) $42,000,000

more important saving, if one considers the capital and operating cost of new aluminum capacity. The cost of new aluminum capacity at $1750/annual ton for the 48,000 tons of increased output from this plant would involve a capital expenditure of $84 million and the production cost of aluminum from a new smelter including return on investment, would be $1181/ton.

(9) Technical Considerations

The degree of technical risk is minimal. The cathode life is the big risk so that cathode life and performance will have to be demonstrated on a number of commercial cells before large numbers of pots are retrofitted. This will take some time, but the development could be very important and dramatic to the aluminum industry.

(10) Effect on Intermediate and Final Products

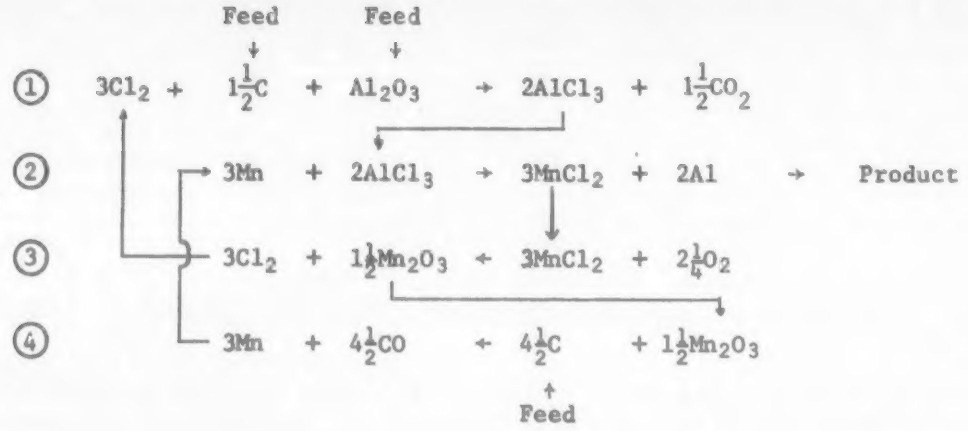
There would be no anticipated effect on the intermediate or final products - cast sows semifinished or finished forms.

c. Toth Aluminum Process

Dr. Charles Toth, Board Chairman of Toth Aluminum Corporation (TAC), has proposed a pyrometallurgical process for the production of aluminum as a proposed competitor to the Hall-Heroult electrolytic reduction process. The basis of the process is the reduction of aluminum chloride with manganese metal, forming manganese chloride and aluminum. The sequence of chemical or pyrometallurgical reactions involved in the process is presented below:

Toth Aluminum

Reaction Sequence


Feed
Feed
① $3Cl_2 + 1\frac{1}{2}C + Al_2O_3 \rightarrow 2AlCl_3 + 1\frac{1}{2}CO_2$
② $3Mn + 2AlCl_3 \rightarrow 3MnCl_2 + 2Al \rightarrow$ Product
③ $3Cl_2 + 1\frac{1}{2}Mn_2O_3 \leftarrow 3MnCl_2 + 2\frac{1}{4}O_2$
④ $3Mn + 4\frac{1}{2}CO \leftarrow 4\frac{1}{2}C + 1\frac{1}{2}Mn_2O_3$
Feed

This is an interesting reduction sequence in which the net overall reaction is $Al_2O_3 + 7.5C + 2.25O_2 \rightarrow 2Al + 7.5CO$. Recently Toth informed his stockholders that the firm had experienced difficulty in carrying out Reaction 2, i.e., the reduction of aluminum chloride with manganese to form manganese chloride and aluminum metal. They have found that it was difficult to completely utilize the manganese metal and that the resulting aluminum product was contaminated with manganese metal. They indicated that the reaction would go to the extent that 80% of the manganese metal is consumed, but that 20% remains unreacted and thus represents a contamination of the aluminum product. Since, at the present time, TAC is no longer offering this process until more research is completed, no detailed consideration was given to this process in this study. The descriptive material on the Toth aluminum process that follows is included for those interested in the conceptual details of the process.

(1) Chlorination of Alumina

Reaction (1) involves the chlorination of alumina in the presence of carbon to form aluminum trichloride, carbon monoxide and carbon dioxide. This step in the process has been operated commercially at 1650°F in a fluidized bed reactor with an alumina feed. Any sodium present would also be chlorinated and would be volatilized, as indicated in recent Alcoa patents, forming a mixed $NaCl \cdot AlCl_3$ salt soluble in $AlCl_3$. Since the sodium present in Bayer alumina is small, the formation of the double salt is not considered a serious problem.

We anticipate that the alumina feed would be preheated, but that the reaction would be at least slightly exothermic even if the reaction took place in the presence of excess carbon so that the off-gases were largely carbon monoxide.

The aluminum trichloride, of course, volatilizes and can be recovered by condensation at about 200°F.

(2) Reduction of Aluminum Chloride with Metallic Manganese

The next step in the sequence is the reaction between aluminum trichloride and manganese metal to form manganese chloride and product aluminum metal. This reaction would probably be carried out in liquid aluminum chloride at about 575°F and 200 psig. It is believed that an excess of aluminum chloride would be required to completely utilize the manganese, if possible. Particles of metallic aluminum produced by this reaction would be separated from the manganese chloride and excess aluminum chloride by some means as yet unspecified.

(3) Oxidation of Manganese Chloride to Manganese Oxide and Chlorine for Recycle

The next step in the process is Reaction (3) in which manganese chloride is oxidized to manganese sesquioxide with liberation of chlorine for recycle. This could be carried out in a fluid-bed reactor operating at 1100°F in which solid manganese chloride is contacted with oxygen. Gaseous chlorine and solid Mn_2O_3 would be the reaction products.

(4) Reduction of Manganese Oxide to Manganese Metal for Recycle

The final step in the operation is the reduction of manganese sesquioxide with carbon back to manganese metal, which of course is recycled to Reaction (2). Originally, it was proposed to carry out this reduction in a blast furnace in which the manganese sesquioxide would be reduced to manganous oxide (MnO) by heat, or carbon monoxide, with the resulting manganous oxide reduced by coke to the metal with the evolution of CO. The procedure has since appeared to be difficult, and it is now anticipated that the reduction of the manganese sesquioxide would more logically be carried out in a submerged arc electric reduction furnace to produce molten manganese metal which would be cooled and recirculated to the aluminum generator.

d. Combination of the Clay Chlorination Process and the Alcoa Chloride Process

(1) Basis of Analysis

An interesting combination is one involving aluminum chloride produced from clay via a clay chlorination process concept as direct aluminum chloride feed to new Alcoa chloride electrolysis cells for production of aluminum. As an example of a clay chlorination process, we used the Toth alumina process. In this analysis we sized the Toth process installation for clay chlorination to produce sufficient aluminum chloride feed to the Alcoa chloride electrolytic cells to produce 160,000 ton/yr of primary aluminum. This means the Toth clay chlorination installation would be sized at a capacity of 44% of the 700,000 ton/yr plant discussed earlier. Toth alumina from the clay process was discussed earlier in this chapter for production of alumina for consumption in conventional Hall-Heroult aluminum smelters. This smaller capacity installation of the Toth process to match a nominal size aluminum smelter requirement for aluminum feed represents a cost penalty, since there is an economic benefit to large-scale recovery of alumina from aluminum-bearing raw materials. This is supported by the fact that new Bayer process installations are much larger in terms of production capacity than the typical older Bayer process plants presently operating in the United States.

(2) The Combined Process Operations

In this combination, the Toth clay chlorination process originally conceived for production of alumina from clay replaces the aluminum chloride feed preparation part of the Alcoa chloride process in which pot feed alumina is chlorinated in the presence of carbon to yield the aluminum chloride feed to the Alcoa chloride cells.

The operation of the feed preparation part of this combination process differs slightly from that of the Toth alumina process described earlier in the following respects.

Since aluminum chloride is required instead of alumina as feed to the cells, the reoxidation of aluminum chloride is eliminated from the operation which reduces the oxygen requirements significantly. The feed to the cells comes directly from the final distillation separation of ferric chloride from the aluminum chloride, as described in detail previously in this chapter of the report.

The operation of the cell feed preparation section of this combination process differs very significantly from the cell feed preparation section of the Alcoa chloride process described in detail earlier. Instead of pot feed alumina, the starting raw material is clay. Instead of a heavy oil coked on the alumina particles, the reductant is coke. Because of the larger volume of impurities in the clay, as compared with the high-purity alumina feed, the feed preparation is more complicated, requires more separation steps, and produces a byproduct titanium dioxide. The feed preparation section of this combination process involves all the steps of the Toth alumina-from-clay process up to the final oxidation of the aluminum chloride to alumina.

(3) Effluent Control

This combination process has all of the effluent control problems of the Toth alumina process, plus some of the effluent control problems of the Alcoa process, viz., those originating from the chloride cell operation. Details on these problems and their costs are found in the sections of this report dealing with the Toth and Alcoa processes.

(4) Energy Use

This combination process consumes 10,637 kWh per ton of aluminum which is much lower than the electric power consumption of 15,600 kWh per ton of aluminum used in existing Hall-Heroult smelters, but higher than the 10,500 kWh per ton of aluminum required in the Alcoa chloride process. This combination process requires coal and coke amounting to 48.5 x 10^6 Btu per ton of aluminum which is significantly higher than the purchased feed for a new Bayer-Hall-Heroult process of 38.6 x 10^6 Btu/ton.

The total energy consumed by this combination process converted to a fossil fuel basis, i.e., considering the inefficiencies of power generation, would amount to 160 x 10^6 Btu/ton of aluminum. This compares favorably with the existing Hall-Heroult process that consumes 188 x 10^6 Btu/ton. However, if one includes the energy for the production of alumina to make the analysis comparable, the total energy of the combination new Bayer-Hall-Heroult process would amount to 164.6 x 10^6 Btu/ton of aluminum, which is a little higher than the Toth-Alcoa combination estimated at 160 x 10^6 Btu/ton of aluminum.

(5) Economic Factors

In Table IV-21 we have presented our estimates of the operating costs for this combination process for the production of aluminum at capacity of 160,000-ton/yr. Based upon the estimates summarized in Table IV-13, the costs look attractive. The capital cost estimate is based on the cost of the Toth alumina-from-clay process, less the alumina chloride oxidation, scaled to the size needed to supply the Alcoa chloride cells with enough aluminum chloride to produce 160,000-ton/yr of primary aluminum metal.

TABLE IV-21

ESTIMATED PRODUCTION COSTS FOR NEW ALUMINUM PLANT, 1975
(Combination of Toth Alumina and Alcoa Chloride Aluminum Processes)

Product: Aluminum Process: Toth-Alcoa $AlCl_3$ Electrolysis Location: Georgia

Annual Capacity: 160,000 tons Capital Investment (CI): $296,000,000 Annual Production: 160,000 tons

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per Net Ton of Product	$ per Net Ton of Product
VARIABLE COSTS				
Raw Materials				
● Clay (Kaolin)	ton	2.50	5.79	14.48
● Chlorine	ton	125.00	0.08	9.65
● Oxygen	ton	12.00	1.62	19.43
● NaCl	ton	30.00	0.001	0.03
● LiCl	ton	2,000.00	0.001	2.00
Byproduct Credits (Crude TiO_2)	ton	332.00	0.11	-37.16
Energy				
● Purchased Fuel				
Coal	10^6 Btu	0.82	16.31	13.37
Coke	ton	35.00	1.24	42.23
● Electric Power Purchased	kWh	0.015	10,637.00	159.55
Water				
● Process	10^3 gal	0.50	1.54	0.77
● Cooling	10^3 gal	0.05	140.00	7.00
Direct Operating Labor (Wages)	Man-hr	6.50	5.56	36.11
Direct Supervisory Wages	15% Op. Lbr.			5.42
Maintenance Labor (Wages)	Man-hr	6.75	7.62	51.43
Maintenance Supervision (Wages)	15% Mnt. Lbr.			7.71
Maintenance Materials	2.5% of CI			46.25
Labor Overhead	32% of wages			32.21
Misc. Variable Costs/Credits				11.00
● Other Operating Supplies				11.39
TOTAL VARIABLE COSTS				432.87
FIXED COSTS				
Plant Overhead	60% of wages			60.39
Local Taxes and Insurance	2% of CI			37.00
Depreciation	7.1% of CI			131.35
TOTAL PRODUCTION COSTS				661.61
Return on Investment (Pretax)	20% of CI			370.00
Pollution Control				37.35
TOTAL				1,068.96

We estimated the cost of the chloride cell installation based upon recent experience with the conventional magnesium cells in which magnesium is produced by electrolysis of magnesium chloride to molten magnesium and byproduct chlorine for recycle, as would be the case with the Alcoa chloride process cells. These estimates are speculative; neither the Toth alumina-from-clay process nor the Alcoa chloride aluminum process has yet been built or operated on a commercial scale. Moreover, the details of both of these processes are very limited, so that the accuracy of the estimates is speculative. However, based on these estimates, it would appear that the operating costs would be higher, $1,069/ton of aluminum, than from an existing Bayer-Hall-Heroult operation ($742/ton) or for an existing Hall-Heroult smelter modified with titanium diboride cathodes ($733/ton). However, the costs are estimated to be lower than for a new conventional Hall-Heroult smelter which would produce aluminum at an estimated $1,181/ton of aluminum, including return on investments, or a new Alcoa chloride process starting with Bayer alumina, ($1123/ton aluminum) when starting with bauxite at $125.00/ton. Bauxite produced in a new facility is estimated to cost significantly more and further improves the relative potential economics of clay chlorination with the Alcoa process.

(6) Status of the Process

This combination process has no formal status, although we have heard that Alcoa has talked with TAC, but we have no information on any arrangement or understanding. The technology of the Toth alumina process, the cell feed preparation section of this combination process, is complicated; much more complicated than the cell feed preparation section of the Alcoa chloride process with its starting raw material, high-purity Bayer alumina. It would appear that Alcoa would prefer to start with a simpler process, starting with high-purity alumina.

4. Summary of Production Costs and Energy Requirements for Production of Aluminum

Table II-3 summarizes the costs and the energy consumption (on a fossil fuel equivalent basis) for producing aluminum in the existing and new Hall-Heroult electrolytic smelting plants and by the alternative Alcoa process. Costs for the new Alcoa process must be compared with new Hall-Heroult smelters, because it is obvious that no new plant could hope to compete with existing plants. On the other hand, since the refractory hard metal cathodes could be retrofitted in existing Hall-Heroult smelters, cost comparisons for this option should be made with both existing and new plants.

While the costs of pollution control are not significant in the cost of producing alumina, as discussed earlier, they are significant, almost 4%, in the cost of producing aluminum from a new facility and 6% in an existing plant. The Alcoa plant has the potential for reducing pollution control costs since the use of fluoride compounds is eliminated.

V. IMPLICATIONS OF POTENTIAL PROCESS CHANGES IN THE ALUMINA/ALUMINUM INDUSTRY

A. PRODUCTION OF ALUMINA BY ACID LEACHING OF KAOLIN CLAYS

1. Impact on Pollution Control

a. Nitric Acid and Hydrochloric Acid Clay Leaching Processes

The application of either of these two processes would present an impact on the environment as a result of producing solid and liquid wastes containing soluble nitrates or chlorides. The solid wastes largely result from the separation of insoluble materials from the leaching step discharged from countercurrent washing thickeners at the final thickener underflow. This underflow then goes through a filtration step in which the final water washing of the insoluble solid waste occurs. Although this material has been rather carefully washed before discharge, it could still contain some soluble nitrates or chlorides, depending on the process.

In addition to this major discharge, in both processes there is a crystallization step which removes impurities as nitrates or chlorides. To remove these materials from the evaporator crystallizer circuit, a bleed stream must be taken off to maintain the purity of the product alumina. In both processes this bleed stream containing aluminum nitrate or chloride and impurities as nitrates or chlorides is finally treated by decomposition to recover the nitrate or hydrogen chloride value. While aluminum chloride or aluminum nitrate and some of the impurities, such as nitrates or chlorides, are decomposable, chlorides of alkali and alkali earth metals would not be decomposed and nitrates of the alkali metals decompose to nitrites. Nitrates are suspected of being carcinogenic. The nitrates of the alkali earth metals are difficult to decompose completely. Thus, there are likely to be soluble nitrates or chlorides in the solid discharge from these decomposition steps.

Also, it is likely that there will be small gaseous emissions of unrecovered oxides of nitrogen and hydrogen chloride from the acid recovery systems which may have to be removed from the off-gases in small scrubbers using alkali solutions. These result in aqueous solutions of soluble nitrates or soluble chlorides requiring discharge.

The cost of air pollution control will depend on specific location and local regulations. The general location of these clay-based processes logically would be on or along the kaolin belt in the State of Georgia which is an area of high rainfall and high groundwater levels. Since the major pollution control costs will be for methods to prevent leaching of soluble chlorides and nitrates, and since there is no apparent economic value in the leached residues if zero discharge is required, the best solution to the control problem would be to discharge to a disposal tailing pond or dump lined with an impervious membrane. This would represent the maximum costs.

b. Clay Chlorination

In the case of clay chlorination, such as the Toth alumina process, which recovers alumina by chlorination of clay in the presence of carbon, we considered the possible pollution problems that could result from this process.

This is a dry process, i.e., there is no leaching involved; the aluminum chloride is volatilized overhead, along with other chlorides, such as ferric chloride, silicon tetrachloride, titanium tetrachloride, and even some of the sodium present in the clay as sodium chloride. These chlorides are separated by a combination of fractional condensation and distillation to produce separated fractions of aluminum chloride, silicon tetrachloride, and titanium tetrachloride, all of which are oxidized to recover chlorine for recycle to chlorination and the respective product oxides--primarily alumina product and byproduct titanium dioxide--for sale.

There are several solid waste streams from these operations. The primary stream is the bottom discharge of unreacted materials from the chlorination step, i.e., the waste from the clay, which would be primarily silica, but is likely to contain some soluble chlorides as well. This would be a dry material unless slurried for disposal.

A second source of waste results from the separation of aluminum chloride from ferric chloride and sodium chloride. To remove sodium and iron that would build up in the separation system, a bleed stream containing ferric chloride, sodium chloride, and some aluminum chloride would be taken off. This stream would be oxidized to recover chlorine before final discharge, but the final discharged product would be iron oxide and alumina plus sodium chloride, and possibly other soluble chlorides as a result of incomplete oxidation during chlorine recovery.

A third source of waste would result from the oxidation of the separated silicon tetrachloride to silica. TAC anticipates that some of this silica might be sold, but most is likely to be waste which could contain soluble chlorides and fine particulates that are likely to be slow to settle.

TAC proposes that the titanium tetrachloride be fully recovered and oxidized to obtain chlorine for recycle and a crude titanium dioxide for sale so that this would not be a waste stream. We believe that complete sale of titanium dioxide is possible because there is a market in the United States, even for a crude titanium dioxide for reprocessing to pigment.

In addition to the above solid wastes, there would be liquid wastes from scrubbing off-gases. The major possible source of gaseous emissions is the off-gas from chlorination after final low-temperature condensation of the silicon and titanium tetrachlorides. The final tail gas would contain carbon monoxide and dioxide, some hydrogen chloride, and possibly some uncondensed silicon tetrachloride which would hydrolyze. These undesirable gaseous emissions could be removed by caustic or lime water scrubbing which would result in carbonates and soluble chloride salts.

We have very little detailed information on these waste streams. The cost of environmental control would depend on site location and local regulations. However, if zero discharge is required, we believe again that the best solution would be to discharge to a disposal tailing pond or dump lined with an impervious membrane. This would represent the best available technology. Of course, other, more esoteric treatments might be necessary in certain locations, but these might make the process totally uneconomical.

c. Summary of Pollution Control Costs

We estimate the maximum cost for pollution control, i.e., for zero discharge, for the clay-based processes compared with the Bayer bauxite-based processes to be as follows:

POLLUTION CONTROL COSTS PER NET TON OF ALUMINA

Bayer	Hydrochloric Acid	Nitric Acid	Toth Chlorination
$1.40	$5.00	$19.00	$10.80

2. Energy Requirements

A comparison of energy requirements for the present Bayer alumina process and the nitric acid, hydrochloric acid, and Toth chlorination processes for the production of alumina are presented below:

ENERGY CONSUMPTION

10^6 Btu per Net Ton Alumina

	Bayer Alumina Bauxite	Hydrochloric Acid Leaching Clay	Nitric Acid Leaching Clay	Toth Chlorination Clay
Process				
Power - kWh/ton	275	134	139	333
Fuel - 10^6 Btu/ton	11.64	37.8	25.3	25.09
Total - Fossil fuel basis (10^6 Btu/ton)	14.53	39.2	26.8	28.6
Pollution Control (10^6 Btu/ton)	0.05	0.02	0.7	0.3

Thus, it can be seen that the clay-based processes, if implemented, would have an important upward impact on energy consumption, as compared with the Bayer process which is the present technology. However, other political and technical advantages will contribute to the decision.

3. Factors Affecting the Possibility of Change

The major factor that would affect the possibility of change in clay processing to produce alumina is the degree of concern that the U.S. aluminum industry has with respect to the major dependence on foreign sources of aluminum-containing raw materials. Also the concern that the government might have with the resulting effect on foreign exchange is a factor.

As prices of foreign bauxite and alumina increase, foreign exchange requirements would increase and interest in clay as a source of alumina would also increase. The development of domestic clays would be enhanced if the depletion allowance on clay were increased.

B. PRODUCTION OF ALUMINUM BY THE NEW ALCOA PROCESS AND BY THE RETROFITTING OF TITANIUM DIBORIDE CATHODES TO THE CELLS

1. Impact on Pollution Control

a. Alcoa Process

The new Alcoa process presents different pollution problems as compared to those of the present Hall-Heroult aluminum smelting process. First, with respect to the molten salt electrolysis cells, the chloride cells would be fully covered to avoid loss of chlorine from the anode which is recycled to the chlorination step. It is likely that the cells would be operated under slight positive pressure to avoid in-leakage of air or moisture. Oxygen in any form is undesirable in the cells and results in the formation of oxides that drop out on the molten aluminum cathode as sludge that reduces the efficiency of the cathode. As a result, it is possible that a small amount of chlorine may leak out of the cell hoods at points where aluminum chloride is charged, but the incentive is there to avoid losses of chlorine. However, with proper hooding, the volume of gas to be handled from the cell room would be less than from the open Hall-Herout cells.

The system is quite different from the present Hall-Heroult cells where crust-breaking is required and fluoride emissions occur. The Alcoa cells are more like magnesium cells in which no crust-breaking is required and where chlorine is removed at the anode. Carbon cathodes are also used, but are inert, which means that no significant amount of carbon oxide gases is released at the anode from the Alcoa cells.

The major air pollution source would be from the coker and chlorinator off-gases. The coker in which fuel oil is cracked on the hot alumina would result in an off-gas containing some cracked hydrocarbon gases and hydrogen sulfide. Since these gases are subsequently burned to provide heat for coking, the off-gas would have to be provided with facilities for SO_2 control.

The off-gas from the chlorinator in which volatile aluminum chloride is produced from alumina and coke would also contain carbon monoxide and carbon dioxide. This gas would be subjected first to high-temperature condensation to remove sodium chloride and unreacted alumina, but also some aluminum chloride. This high-temperature condensate would be oxidized to recover chlorine for recycle and would produce a solid waste of alumina and sodium chloride; the sodium chloride would be removed by leaching to yield alumina for recycle to the chlorinator. This treatment would result in a waste aqueous stream of sodium chloride.

The remaining gas, containing most of the aluminum chloride, would then be subjected to low-temperature condensation to remove the aluminum chloride as solids that would be charged to the cells. The remaining non-condensable gases would consist largely of carbon monoxide, carbon dioxide, hydrogen chloride, and possibly also some chlorinated hydrocarbons. The hydrogen chloride results from moisture present in the chlorinator feed that would be converted in the presence of carbon and chlorine. It would be removed from the off-gas to produce byproduct hyrdochloric acid. After scrubbing with sodium hydroxide to remove any remaining hydrogen chloride, the end-gas would be incinerated by burning the remaining combustible gas, primarily carbon monoxide, in a combustion chamber.

The major pollution control costs would be to reduce gaseous emissions i.e., hydrogen sulfide or SO_2, depending on whether the sulfur removal was before or after burning the off-gas from the coker control and hydrogen chloride emissions from the chlorinator off-gas.

The latter control, i.e., hydrogen chloride, would result in a liquid waste stream containing sodium chloride. In addition, there would be a sodium chloride-containing aqueous waste stream for the discharge of sodium contained in the alumina. There would also be salts and sludges removed from the cells to remove impurities periodically. It is likely that if these discharges contain much lithium chloride, they would be treated to recover this expensive salt for reuse and would result in an additional sodium chloride waste stream.

Considering the above, we estimate that the cost of pollution control would amount to $12.44/ton of aluminum produced. If the sodium chloride stream would have to be totally impounded, the costs would be $0.50 to $1.00/ton as a result of installing a tailing pond lined with an impervious barrier. This would depend on the specific location and local regulations.

b. Application of Titanium Diboride Cathodes to Existing Hall-Heroult Cells

These cathode materials, applied in existing plants, would not change the pollution problems significantly; if anything, they might slightly reduce the problem for the following reasons.

The consumption of, and therefore the production of, anode carbon would be slightly less and thus the pollution, as a result of making anodes, would be less. The volume of off-gas per ton of aluminum would be less from the anode production and baking. The volume of off-gas from the cells would also be less per ton of aluminum, but the concentration of fluoride in the off-gas would be higher. However, the fluorides leaving the cell should remain about the same per ton of aluminum produced.

All of the above effects result from reducing the back reaction of the anode so that the off-gas from the anode would be largely carbon dioxide and less carbon monoxide. Since carbon dioxide takes more oxygen from the alumina than is the case with carbon monoxide, there is less carbon consumed, and the volume of cell off-gas is less per ton of aluminum. However, if the cells were to be operated to produce 30% more aluminum as expected, the gas flow of the cells would be about the same as before without the installation of the cathodes. The cost of off-gas handling would be reduced. The cost of reagents to remove the fluorides would remain the same per ton of aluminum produced.

The net result is that we would expect existing air pollution control systems in present smelters to be adequate to handle the effects of the installation of titanium diboride cathodes in existing plants and that the cost of control would be no higher and, if anything, slightly lower than in the present Hall-Heroult smelters per ton of aluminum, as detailed in Appendix C. Pollution problems created by the manufacture of the diboride electrodes have not been considered because there is no information on the process used to produce the titanium diboride cathodes.

c. Summary of Anticipated Control Costs

We estimate pollution control investment and operating costs for the new Alcoa process and the application of titanium diboride cathodes on the existing aluminum smelters would be as shown in Tables IV-14 and IV-15.

In addition, it should be recognized that if power consumption per ton of aluminum can be reduced by 20-30%, there are additional favorable effects on the pollution problems. If power consumption is reduced, the production of power is less, which means less fly ash and less SO_2 per ton of aluminum. This also means less coal mined and a reduction of the magnitude of the environmental problems relating to coal mining, all in proportion to the reduction.

2. Energy Requirements

A comparison of energy requirements for the present Hall-Heroult process and the Alcoa chloride process and the application of titanium diboride cathodes to existing cells is presented below:

ENERGY CONSUMPTION

10^6 Btu/Net Ton Aluminum

	Existing Hall-Heroult Smelters	Alcoa Chloride Process	Existing Hall-Heroult Smelters TiB_2 Cathodes
Power - kWh/ton	15,600	10,500	12,480
Fuel - 10^6 Btu/ton	24.02	24.85	20.14
Total Fossil Fuel Basis 10^6 Btu	187.82	135.10	151.18
Pollution Control 10^6 Btu/ton	1.71	0.42	1.31

It is obvious from the above that the incentive is to reduce energy consumption, and the concomitant effect would be to reduce pollution problems and costs.

3. Factors Affecting the Possibility of Change

The incentive for the reduction in power consumption is enough to favorably affect the chances of change in the reduction of alumina to aluminum in the U.S. industry. The incentive will be increased as power costs increase, without any additional pressure or effects that Federal agencies of the Government could bring to bear on the situation. Thus, we believe that the potential for change to these lower energy-consuming alternatives for the production of aluminum will depend entirely upon the results of the research and the capital costs involved in making the necessary changes.

C. AREAS OF RESEARCH

Probably the most promising area of research that would have the greatest immediate effect on energy consumption and environmental problems would be the introduction of titanium diboride cathodes in the existing plants. The research and development work that is most important relates to the quality of the titanium diboride cathodes. This is a materials problem that might justify some Government-sponsored research or some funding to expand present research. The materials research that is being carried out relating to this problem is largely being done by the private sector, companies that are interested in titanium diboride cathodes. These would include Kawecki Berylco Industries, Inc., PPG Industries, Inc., and, in the past, Carborundum, Union Carbide Corporation, and Norton. The present leaders in this field appear to be PPG and Kawecki Berylco. The research that has been done is largely related to preparing and testing materials in aluminum cells. It is more trial and error and adjustment research, with the real problem that of demonstrating extended cathode life. The payoff here would be large in maintaining the aluminum industry in a healthy position to permit further expansion in the United States. This would reverse the trend toward exporting technology and production to areas where power is available at low cost.

The other area of research opportunity is a continuation of the Bureau of Mines' recent efforts on developing means for producing alumina from domestic raw materials, particularly kaolin and anorthosite clays. The situation could be improved with respect to slowing the increasing cost of bauxite and alumina imported from abroad, if it could be demonstrated on a sizable production unit that the United States could produce alumina from its own domestic sources. This would tend to deter future increases in taxes on bauxite and the foreign exchange problem related to importation of alumina-bearing raw materials. More specifically, we believe, because we have seen the results of recent work on the nitric acid process, that much more of the thermal requirements for these processes could be supplied by burning coal instead of natural gas.

Of course, as mentioned previously in this report, the development of domestic reserves of alumina-based materials would be enhanced if the depletion allowance on clays were increased.

Regrettably the clay processes, acid leaching, or the chlorination process appear to offer no energy incentive over the existent Bayer process.

APPENDIX A

INDUSTRY STRUCTURE - ALUMINUM

1. DESCRIPTION

The aluminum industry is comprised of two basic sectors: (1) the production of alumina from bauxite by the Bayer process, and (2) the reduction of alumina to aluminum metal by the Hall-Herouit electrolytic reduction process. These two operations are conducted at entirely separate locations.

a. Alumina

Within the United States there are nine alumina production plants (see Figure A-1). Eight of these are located in the continental United States and the ninth is in the Virgin Islands on the island of St. Croix. Total alumina production capacity of the industry is estimated at 7.7 million short tons with individual plant capacities ranging from 1.385 million short ton/yr (Reynold's Corpus Christi plant) to 370,000 short ton/yr (Martin Marietta's plant at St. Croix) (see Table A-1). By modern standards the U.S. alumina plants are considered small. Most new installations being built abroad start at at least 1 million and more typically 2 million ton/yr capacity.

With the exception of the plant at St. Croix, which was built in the 1960's, all of the present U.S. alumina plants are relatively old. The oldest plant was built by Alcoa at Mobile, Alabama, in 1940; two more (Kaiser at Baton Rouge and Reynolds at Hurricane Creek) were built prior to 1946, and the rest began operating in the late 1940's and early 1950's.

Most of the alumina plants are located on the Gulf Coast because of the availability of natural gas. The two plants in Arkansas, at Hurricane Creek and Bauxite, were originally based on Arkansas bauxite, the only domestic source of this raw material. As the quality of Arkansas bauxite has become poorer, these plants have turned to foreign sources for part of their bauxite supply.

Some alumina plants are located near aluminum smelters. At Point Comfort, Texas, for example, Alcoa has both an alumina plant and an aluminum smelter. The Reynolds alumina plant in Corpus Christi serves Alcoa's Texas smelters as well as the Reynolds smelter in Corpus Christi. Sources of alumina are therefore not always captive. Foreign alumina plants are often under joint ownership. Since the establishment of a new alumina plant involves a major investment in mining and production facilities, it is often organized on the basis of pay-or-take contracts with aluminum producers. Plants are not usually designed and constructed until firm long-term commitments have been obtained for marketing the alumina.

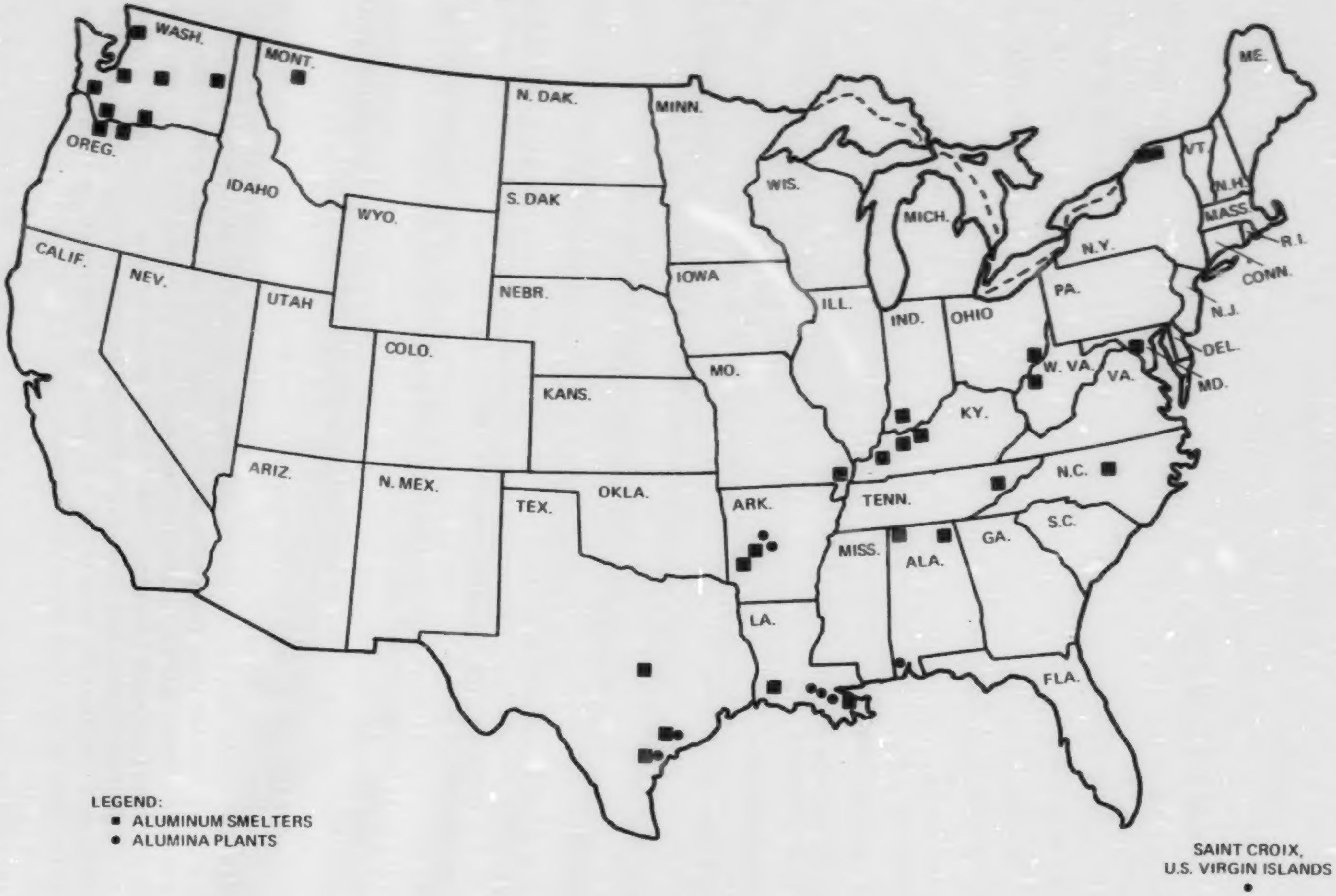

WASH.
OREG.
CALIF.
NEV.
IDAHO
MONT.
WYO.
UTAH
ARIZ.
COLO.
N. MEX.
N. DAK.
S. DAK
NEBR.
KANS.
OKLA.
TEX.
MINN.
IOWA
MO.
ARK.
LA.
WIS.
ILL.
MICH.
IND.
OHIO
KY.
TENN.
MISS.
ALA.
GA.
FLA.
S.C.
N.C.
VA.
W. VA.
PA.
N.Y.
VT.
N.H.
ME.
MASS.
R.I.
CONN.
N.J.
DEL.
MD.
LEGEND:
■ ALUMINUM SMELTERS
● ALUMINA PLANTS
SAINT CROIX,
U.S. VIRGIN ISLANDS

Figure A-1. Location of Alumina Plants and Aluminum Smelters in the United States

TABLE A-1

U.S. ALUMINA PLANTS
Location and Capacity - 1975

	Short Ton/Yr
Aluminum Company of America	
Mobile, AL	1,025,000
Bauxite, AR	375,000
Point Comfort, TX	1,350,000
Martin Marietta	
St. Croix, VI	370,000
Kaiser Aluminum and Chemical	
Baton Rouge, LA	1,025,000
Gramercy, LA	800,000
Reynolds Metals Company	
Hurricane Creek, AR	840,000
Corpus Christi, TX	1,385,000
Ormet Corporation	
Burnside, LA	600,000
	7,770,000

b. Aluminum

There are 31 aluminum plants in the United States, operated by 12 companies, 6 of which are also domestic alumina producers. These plants are located primarily in three areas: along the Mississippi and Ohio Rivers, in the Pacific Northwest, and in upper New York State at or near Massena, N. Y. (see Figure A-1). Total aluminum production capacity in 1975 (see Table A-2) is estimated at 5,019 million short tons, with individual plant capacities ranging from 285,000 (Alcoa's plant at Rockdale, Texas) to 36,000 short ton/yr (Consolidated Aluminum's Lake Charles, Louisiana plant).

The location of aluminum smelters is determined by two factors: access to river systems for transportation of alumina and availability of what was originally low-cost power. Plants in Missouri, Kentucky, Indiana, Ohio, West Virginia, Tennessee, North Carolina, and Alabama take advantage of both the Mississippi-Ohio River transport system and the availability of low-cost coal. The two plants in Massena, New York, have access to the St. Lawrence River for transportation and low-cost hydroelectric power. Plants located in Washington (7 plants), Oregon (2 plants), and western Montana (1 plant) are also located near hydroelectric power.

Nine of the 31 smelters began operation prior to 1946 (see Table A-3). Ten years later there were a total of 15 plants in operation, and by 1970, 11 more had begun producing aluminum. Soderberg and prebake smelters were

TABLE A-2

U.S. ALUMINUM PLANTS (1)
Location and Capacity - 1975

Aluminum Company of America(2)	Short Tons/Year
Alcoa, TN	270,000
Badin, NC	120,000
Evansville, IN	280,000
Massena, NY	140,000(3)
Point Comfort, TX	180,000(4)
Rockdale, TX	285,000
Vancouver, WA	115,000
Wenatchee, WA	190,000(5)
Anaconda Aluminum	
Columbia Falls, MT	180,000
Sebree, KY	120,000
Consolidated Aluminum	
New Johnsonville, TN	141,000
Lake Charles, LA	36,000
Martin Marietta	
The Dalles, OR	90,000
Goldendale, WA	115,000(6)
Eastalco	
Frederick, MD	174,000(7)
Intalco	
Bellingham, WA	260,000
Kaiser Aluminum and Chemical	
Chalmette, LA	260,000
Mead, WA	220,000(8)
Ravenswood, WV	163,000
Tacoma, WA	81,000
Ormet	
Hannibal, OH	260,000(9)
Noranda	
New Madrid, MO	70,000
National Southwire Aluminum	
Hawesville, KY	180,000
Revere Copper and Brass	
Scottsboro, AL	114,000(10)
Reynolds Metals Company	
Arkadelphia, AR	68,000
Corpus Christi, TX	114,000
Jones Mills, AR	125,000
Listerhill, AL	202,000
Longview, WA	210,000
Massena, NY	126,000
Troutdale, OR	130,000
	5,019,000

TABLE A-2

U.S. ALUMINUM PLANTS
Location and Capacity - 1975 (Cont.)

Footnotes:

1. Unless otherwise indicated, no change in capacity between 1974 and 1975.
2. Total capacity for company in 1974 was 1,575,000 short tons/year. 1975 figures will be higher.
3. 1974 - 135,000 short tons/year. Increase due to improvements.
4. 1974 - 185,000 short tons/year. Decrease based on company report. No further explanation available.
5. 1974 - 180,000 short tons/year. Increase due to improvements.
6. Bureau of Mines revised up to this figure from 111,000 short tons/year for both 1974 and 1975.
7. 1974 - 88,000 short tons/year. Substantial increase due to possible take-over by Alumax and addition of second pot line.
8. Bureau of Mines revised up to this figure from 206,000 short tons/year for both 1974 and 1975.
9. 1974 - 250,000 short tons/year. Increase due to improvements.
10. 1974 - 112,000 short tons/year. Increase due to improvements.

Source: Bureau of Mines, Personal Communication.

TABLE A-3

U.S. ALUMINUM SMELTERS - AGE AND TECHNOLOGY

Company & Location of Smelter	Age	Smelter Technology[1]
Aluminum Company of America		
Alcoa, TN	pre-1946	PB
Badin, NC	pre-1946	PB
Evansville, IN	1960	PB
Massena, NY	pre-1946 & 1958	PB
Point Comfort, TX	1950	VSS
Rockdale, TX	1952	PB
Vancouver, WA	pre-1946	PB
Wenatchee, WA	1952	PB
Anaconda Aluminum		
Columbia Falls, MT	1955	VSS
Sebree, KY	1973	-
Consolidated Aluminum		
New Johnsonville, TN	1971	PB
Lake Charles, LA	1971	-
Martin Marietta		
The Dalles, OR	1958	VSS
Goldendale, WA	1971	-
Eastalco		
Frederick, MD	1970	PB
Intalco		
Bellingham, WA	1966	PB
Kaiser Aluminum		
Chalmette, LA	1957	HSS
Mead, WA	pre-1946	PB
Ravenswood, WV	1957	PB
Tacoma, WA	pre-1946	HSS
Ormet		
Hannibal, OH	1958	PB

TABLE A-3

U.S. ALUMINUM SMELTERS - AGE AND TECHNOLOGY (Cont.)

Noranda		
New Madrid, MO	1971	PB
Revere Copper & Brass		
Scottsboro, AL	1970	PB
Southwire		
Hawesville, KY	1969	PB
Reynolds Metals Company		
Arkadelphia, AR	1952	HSS
Corpus Christi, TX	1952	HSS
Jones Mills, AR	pre-1946	PB
Listerhill, AL	pre-1946	HSS
Longview, WA	pre-1946	HSS
Massena, NY	1959	HSS
Troutdale, OR	1959	PB

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[1] PB = Prebaked
HSS = Horizontal Soderberg System
VSS = Vertical Soderberg System

built in the 1940's and 1950's, but in the last 15 years only prebake smelters have been constructed.

3. Source of Raw Materials

Since 1.93 tons of alumina are required to produce 1 ton of aluminum, the total alumina requirement of the U.S. aluminum industry, when operating at full capacity, is 9,686,670 tons, 1,916,670 tons more alumina than can be produced domestically. Therefore, at full-capacity operation, 20% of the alumina used in aluminum production would have to be imported from foreign sources, primarily the Caribbean, northern South America, and Australia. Since the only domestic source of bauxite for alumina production is Arkansas bauxite, and since this has become increasingly poor in quality, having a high silica content, virtually all alumina produced in the United States today is based on bauxite imported primarily from the same source countries which also supply alumina.

It is unlikely that new grassroot Bayer alumina plants will be built in the United States to produce the alumina that is presently imported. The bauxite-producing nations have come together in an OPEC-like organization and are pressuring the aluminum companies to locate their alumina-producing operations near the source of the bauxite. This pressure is in the form of local taxes imposed on the bauxite before it is shipped to the United States. (However, local taxes are also imposed on alumina before shipment to the United States, and this is an incentive for U.S. producers to find alternative raw materials within their own country on which to base aluminum production.)

Other incentives for converting bauxite to alumina at the source of the bauxite include a reduction in the freight charges, availability of financing, and lower cost labor in the bauxite-producing countries. Approximately 2 tons of bauxite are required to produce 1 ton of alumina, making shipment of the alumina rather than the bauxite less costly. Moreover, most of the bauxite-producing countries are relatively undeveloped and, as such, are able to secure loans from organizations, such as the World Bank, for the transportation and infrastructure requirements (e.g., ports, roads, housing for workers, etc.) of alumina production facilities unavailable to the United States. For these reasons, current construction of alumina plants is largely overseas, engineered by American, European, and Japanese aluminum producers. The only potential alumina production expansion in the short term in the United States is production based on domestic clay. This would represent a deterrent to increased alumina and bauxite costs as the raw material would be domestically available.

2. ECONOMIC OUTLOOK

a. Consumption

From 1953 to 1973, world consumption of aluminum experienced a long-term growth rate on the order of 10% per year. In the United States, consumption has risen gradually over the years, except in the 1940's when it rose sharply and then leveled off in response to wartime needs for aircraft production.

Aluminum's growth has been due to a variety of factors, which differ in importance for each market and application. In general, these factors involve economics; physical, mechanical, and chemical properties; and esthetics.

Building and construction is the largest end-use for aluminum in the United States, followed by transportation, the electrical industry, packaging, and consumer durable goods. The two fastest growing markets are transportation and packaging.

In the building industry, the two major applications for aluminum are in windows and doors and in external cladding for walls and roofs. Aluminum is used for primary construction and, even more widely, in renovating existing (particularly residential) buildings. The recent growth in mobile homes has benefited aluminum in the building market. The earliest transportation applications for aluminum were in aircraft, and the aerospace industry now accounts for 50% of the total transportation category.

Bare overhead electrical transmission and distribution lines were the first applications in which the substitution of aluminum became a serious threat to another material, in this case, copper. In the world, aluminum has captured this market.

Packaging is the fastest growing major aluminum market. About 50% of the aluminum used in packaging is in cans, including beverage cans, can ends, and composite cans (a combination of paper and aluminum foil). Aluminum is also used for many specialty cans, such as the rapidly growing, shallow-drawn cans for single-portion servings. Aluminum has also been very successful in rigid foil containers. Although aluminum has been substituted for traditional packaging materials in many cases, much of its growth in the packaging market has been attributable to development of new products and methods of packaging.

Aluminum's inroads into the durable goods market have been at the expense of many other materials, primarily steel, wood, zinc, and brass.

Table A-4 shows U.S. aluminum shipments by market for the years 1972, 1973, and 1974 as well as the percentage of total shipments each market accounts for. No significant changes in the market percentages are likely in 1975, although there may be an increase in the use of aluminum in the auto industry. A significant decrease in total shipments is expected, as a reflection of a reduction in demand.

In the 1960's U.S. consumption grew by an average of 8% per year (compared to rates of 4-5% per year for steel, copper, and nickel) and grew from 48% of world consumption in 1960 to 54% in 1965 before dropping back to 48% in 1969 (see Figure A-2). The dominant position of the United States in terms of smelter capacity began to erode during the 1960's, as U.S. capacity fell from 53% of the world total in 1960 to 45% in 1970. The rate of smelter building in the United States dropped from 13% per year in the 1950's to less than 6% per year in the 1960's to 2.5% per year in the first half of the 1970's.

TABLE A-4

U.S. ALUMINUM SHIPMENTS BY MARKET AND PERCENT OF MARKET (000's short tons)

	1972	%	1973	%	1974	%
Building and construction	1,597	27	1,800	25	1,587	22
Transportation	1,112	18	1,404	19	1,225	18
Containers and packaging	905	15	1,028	14	1,125	17
Electrical	768	13	927	13	930	14
Consumer durables	563	9	669	9	578	9
Machinery and equipment	375	6	475	7	500	8
Exports	281	5	470	7	472	7
Other	414	7	435	6	373	5
Totals	6,015	100	7,208	100	6,790	100

Source: Engineering & Mining Journal, March 1975.

The improved profits of the 1950's and the continuing growth of the 1960's brought a number of new companies into the field. As a result, the percentage of industry capacity owned by the three largest U.S. producers - Alcoa, Reynolds, and Kaiser - was somewhat reduced (although still substantial).

Another change has been the growth in international investment by the leading companies. For many years the North American producers obtained raw materials from the United States and the Caribbean and carried out virtually all of their smelting and semifabricating in North America; the European producers used European ore and processing facilities; and both groups concentrated on supplying their respective markets. The remainder of the world had relatively small demand. However, during the 1960's these companies found it necessary to invest abroad at all levels to develop new sources of raw materials and to protect and develop ingot and semifabricating markets. The U.S. producers now have about 15% of their smelter capacity outside the United States.

The financial condition of the aluminum industry is a matter of growing concern. The rapid rate of growth of the industry generated heavy capital requirements. The industry's requirement of $1.50-2.00 of capital investment per dollar of annual sales is about three times the average for all industry. Since a major share of the industry's capital is borrowed, the high cost of money has had a severe impact on aluminum costs.

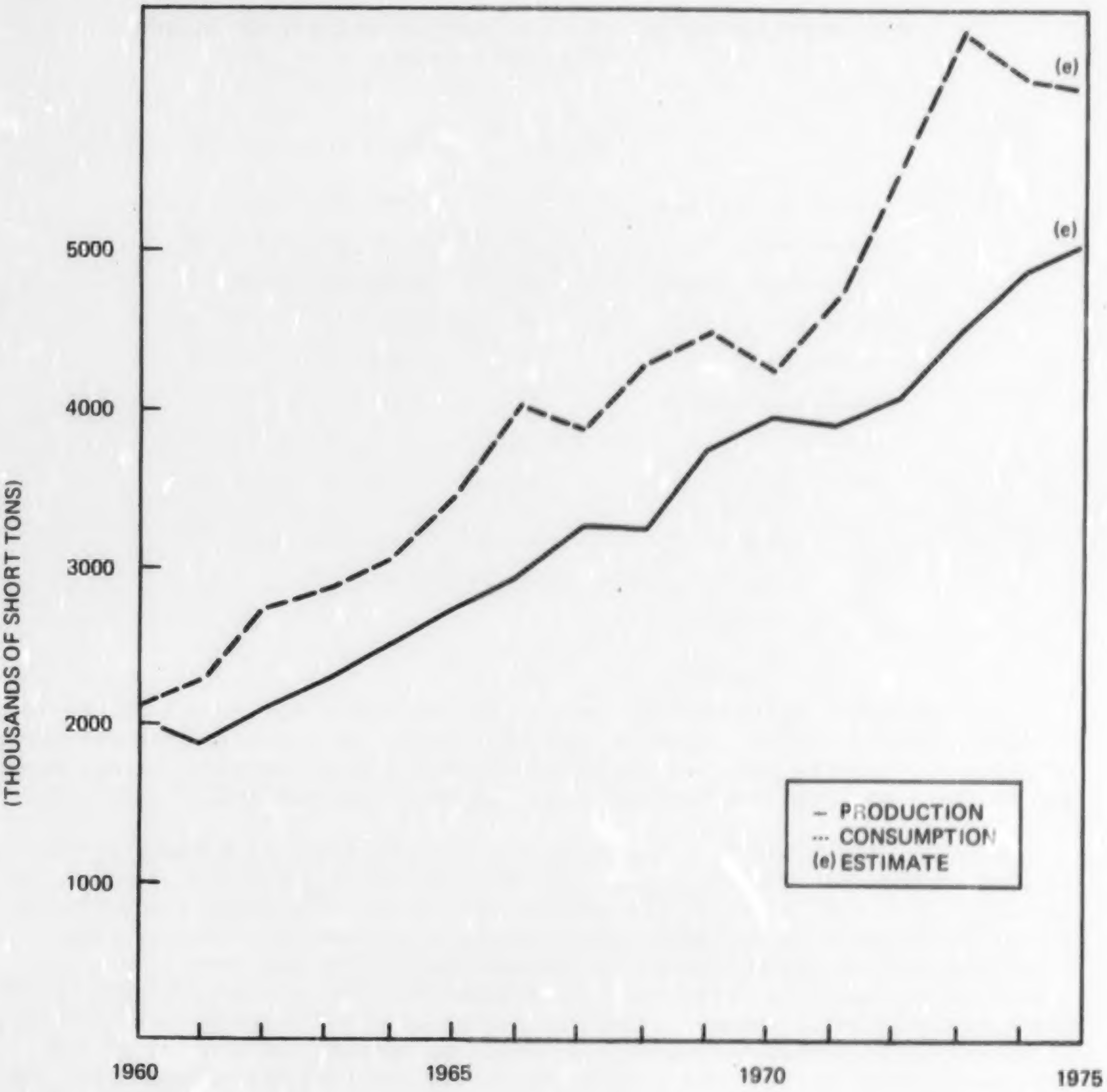


Figure A-2. U.S. Aluminum Production and Consumption - 1960-1975

An unfortunate tendency until at least the mid-1960's was for companies to make smelter investments to maintain market share rather than evaluating the merits of each investment in its own right. The industry expected the healthy profits of the 1950's to reappear. Instead of being concerned about the sizable gaps between anticipated growth in demand and scheduled capacity additions which were evident throughout the decade, the companies continued to compare future demand with present capacity, a perspective which encouraged continued expansion. Posted ingot prices served much the same end, suggesting to outsiders that there were good profits to be made in aluminum smelting. However, actual prices were well below posted prices and returns on investment were well below general industry standards. The industry's overcapacity tendencies have also been spurred by Government economic planners who felt that the national economy would benefit from the existence of aluminum smelters and subsidized companies to build them.

Unfortunately, small surpluses are enough to have substantial price impacts. Heavy capital investment in alumina plants and smelters plus power contracts that often allow for little consumption flexibility give the aluminum industry very high fixed costs, which put great pressure on management to cut prices rather than output. However, the market is relatively price insensitive in the short term, and price cutting serves to reduce total industry revenues rather than to expand the total market.

While the industry reduced smelting costs by roughly 10% during the 1960's, ingot prices in real terms are below their 1960 levels. The United States posted price in constant dollars is lower than in 1960 and in current dollars is only 1¢/lb above the 1960 level.

b. Smelter Economics

The life of an alumina plant is generally very long. Most plants have been expanded and some of the original equipment has been replaced. The life of an aluminum smelter is really the life of a system: buildings, aluminum calcination equipment (rotary kilns, presses, and ovens for making anodes), the electrical equipment, transformers, rectifiers, busbars, cranes, docks, railroad sidings, storage areas, silos, etc.

A cell has a definitive life. Most can operate almost without interruption for three to four years, while more modern cells operate for four to six years. At the end of a cell's life, it is removed from the line and rebricked and rebuilt with new cathodes; i.e., completely refitted within the steel shell. Over a period of 14 to 16 years, even the shells are replaced. Accordingly, most of the original plants have been expanded by an addition of cell lines. This has required increased power capacities and additional busbars, buildings, and facilities for producing anodes.

Until recently, there has been no incentive to reduce power consumption. Aluminum smelters have traditionally been located where power was cheap. In many cases, aluminum smelters were located a considerable distance from markets for aluminum. Today there is no really cheap power left; that which is theoretically cheap is too inaccessible. As a result, freight costs, capital and interest charges, and tariffs have also become important site selection factors.

Although the Hall-Heroult process for the reduction of alumina to aluminum metal has not changed basically since its introduction over 70 years ago, important design and engineering changes have evolved. During the past 40-50 years, commercial cells have increased in size from 8,000 to 170,000 amperes and have diminished 35-40% in power consumption. Modern cell lines are more mechanized, and labor requirements in the cell rooms have been reduced to a minimum. In the 1960's production costs were reduced about 10%, but we believe further reduction will be more limited in the 1970's.

Past improvements resulted from the competitive development of two versions of the Hall-Heroult cell, which differ mainly in the nature of the carbon anode: the Soderberg (continuous self-baking) type and the prebaked type. The early, large (high-amperage) cells used Soderberg anodes because they provided low-current densities (prebaked anodes large enough for high-amperage cells were originally difficult to produce) and the capital cost for a moderate-sized plant was lower. However, industry has since learned how to make large prebaked anodes and is building larger capacity reduction plants. We doubt that any new Soderberg-type plants will be built because of their 2-10% higher power consumption and also because they present more difficult air pollution problems, consume greater amounts of carbon, and are more difficult to control and automate.

Other means of cutting production costs have been under development for a number of years, some of which are discussed in the body of this report.

In addition to the obvious influence of rising power and labor costs, the industry is faced with two other problems that will put upward pressure on production costs. The industry is entirely dependent on synthetic cryolite for use as the reduction electrolyte. This material is produced from fluorspar, which is currently in tightening supply and whose price is increasing because of its growing consumption in steelmaking. Also, aluminum plants have been forced to install air and water pollution controls to eliminate fluoride emissions. Although Alcoa has developed a process that simultaneously eliminates fluoride emissions and produces aluminum fluoride for use in the bath (and will make this method available to other companies who wish to use it), the process would involve new capital costs. We believe the industry will be hard pressed to offset all these higher cost influences by new production economies in the 1970's.

U.S. aluminum smelting and semifabricating operations were relatively unprofitable during the 1960's. Profits were made on raw materials and by companies (principally Alcoa) with low-cost hydropower sources. During the 1970's there will be less opportunity for aluminum companies to acquire new low-cost hydropower sources and growing pressure on raw material profitability. Thus, producers will have to look to smelting and semifabricating for increased profits to compensate for relative declines in other areas. The industry's unsatisfactory earning performance is reflected in the market values of the outstanding stock of the major aluminum companies, which are well below the cost of replacing their smelter capacity alone.

The aluminum industry needs substantially more investment money in the 1970's than it did in the 1960's. Raising capital in the amounts needed will be made more difficult by high interest rates and the industry's lackluster earnings record.

Of the available options for improving profitability, substantial cost reduction does not appear promising, especially in view of rising power costs. While the outlook for alumina prices is clouded, we see no grounds to assume a change that will improve the profitability of the U.S. majors.

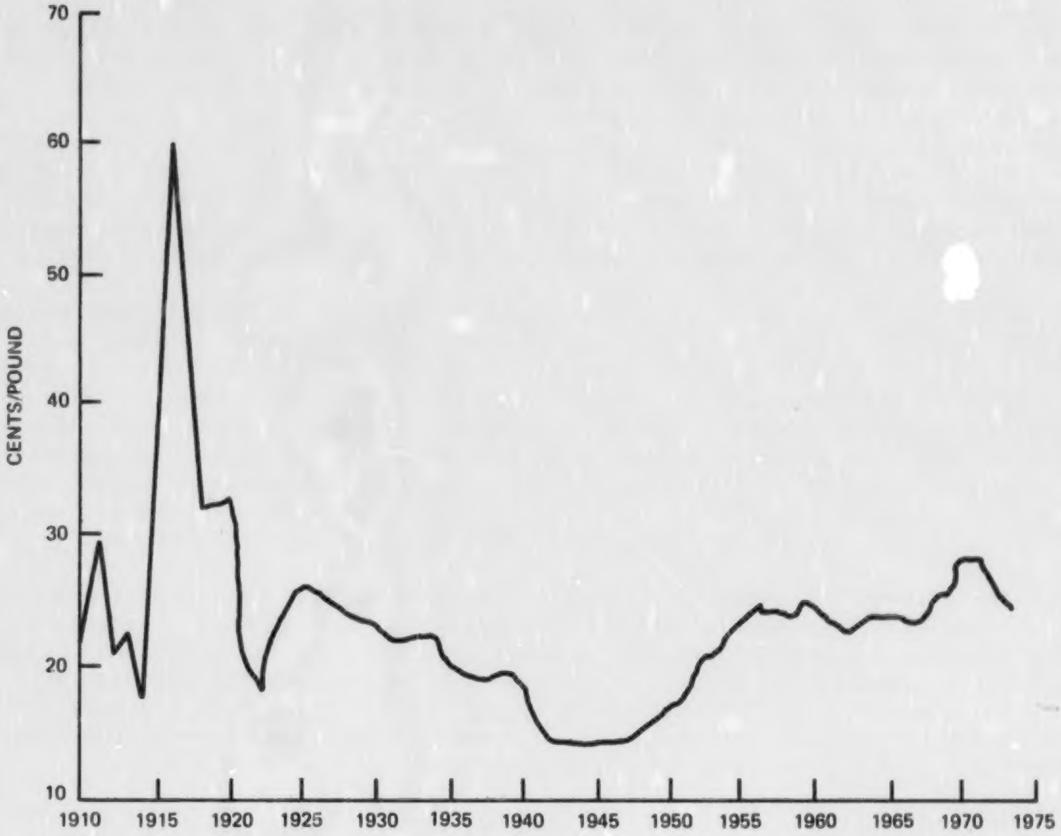
The long-term price level for aluminum (see Figure A-3) is influenced by many, often conflicting pressures, including costs, profit levels, competition with other materials, the international supply-demand balance, and industry competition. The aluminum industry has grown rapidly by making metal available when it was needed and at a price which made it economically attractive to use. If supply were allowed to drop below demand for an appreciable period, list price would fluctuate considerably and some of the incentive to use aluminum would be lost. In applications where aluminum competes with copper, aluminum has historically had an advantage in its relatively stable price.

A number of current trends weigh both for and against higher ingot prices. On the positive side, the industry is showing some signs that it might be better at handling overcapacity than it was in the 1960's. The share of world smelter capacity accounted for by the major North American companies has dropped sharply in recent years and is scheduled to drop even more in the 1970's. This trend suggests that these companies are now concentrating more on the profitability of investments rather than on maintenance of market share. Also, they have shown more willingness to take capacity out of circulation early in an adverse supply/demand trend than has ever been the case before.

The present low earnings performance of the industry will create pressure for higher prices as companies find difficulty in raising money. Unfortunately this natural market force is weakened by the availability of "political" capital in countries where the creation of jobs and industrial activity are more important than the profitability of the project. The industry must do its utmost to convince international loan agencies and governments that smelters should not be built before economic sales outlets are established.

Several negative pressures confront the move to raise ingot prices. The principal one is a projected overcapacity. The 1974-75 downturn in U.S. consumption has created a gap. Despite the significant production cutbacks mentioned earlier, prices have weakened from 1969-1970 levels, and we do not expect prices to improve much until demand picks up substantially.

Another negative factor is the number of independent smelters around the world that may not resist the temptation to emphasize volume rather than price improvement once demand strengthens. Even the major companies will experience difficulty in restraining their production to coincide with consumption.



SOURCE: ENGINEERING & MINING JOURNAL, MARCH 1975

Figure A-3. Annual Average Price Aluminum - 1910-1974

c. Leading Companies

The structure of the world aluminum industry is becoming significantly less concentrated as investments are distributed across more countries and among more companies. The tendency to integrate operations is expected to continue, but will more likely involve large consumers integrating backward rather than ingot producers adding substantially to captive outlets. New participants will probably continue to enter the industry, especially in raw material ventures and in combined smelter/semifabricating facilities. The four major North American aluminum companies - Alcoa, Alcan, Reynolds, and Kaiser - are also the largest aluminum producers in the world.

APPENDIX B

PRESENT TECHNOLOGY

1. RAW MATERIALS

The major raw materials for the primary U.S. aluminum industry are imported alumina and imported bauxite, which is domestically refined to alumina. In addition to these basic raw materials, there is some small production of alumina from alunite based upon a small pilot plant operating at Golden, Colorado. However, for all practical purposes, the alumina for the U.S. market is produced by Bayer process based upon imported bauxite. This is the first step in the domestic primary aluminum industry.

2. DESCRIPTION OF MAJOR PROCESSES

a. Refining of Bauxite to Alumina via the Bayer Process (Figure B-1)

(1) Digestion

In the Bayer process, finely ground bauxite (-35 mesh), usually wet ground in spent digestion liquor, is digested at elevated temperatures under pressure. The digesting liquor contains sodium aluminate and free caustic. In this operation the alumina hydrate in the bauxite is dissolved by the free caustic as sodium aluminate according to the following reaction:

$$Al_2O_3 \cdot xH_2O + 2NaOH \rightarrow 2NaAlO_2 + (x+1)\ H_2O$$

The solubility of alumina (Al_2O_3) increases with temperature and caustic concentration. Bauxites used in the production of alumina contain alumina trihydrate ($Al_2O_3 \cdot 3H_2O$) and alumina monohydrate ($Al_2O_3 \cdot 1H_2O$). Optimum reaction conditions vary with the hydrate type as follows:

Trihydrate: 128-192 g/l NaOH @ 250°-340°F (50-60 psi),

Monohydrate: 257-389 g/l NaOH @ 390°-570°F (up to 500 psi).

The U.S. industry has historically been based on bauxites from the Caribbean which are primarily trihydrates, whereas the European industry has historically been based more on bauxites that are typically much higher in monohydrate. Trihydrate ores are, of course, preferred because of milder operating conditions; however, the use of ores with increasing amounts of monohydrate is becoming necessary in the U.S. and Caribbean alumina plants. The average monohydrate content of bauxites presently imported into the United States is 15-20%. To obtain high alumina recovery from these materials requires higher digestion temperatures and pressures. Digestion temperatures of 400°F and 200 psi are now becoming common in the U.S. Bayer alumina plants.

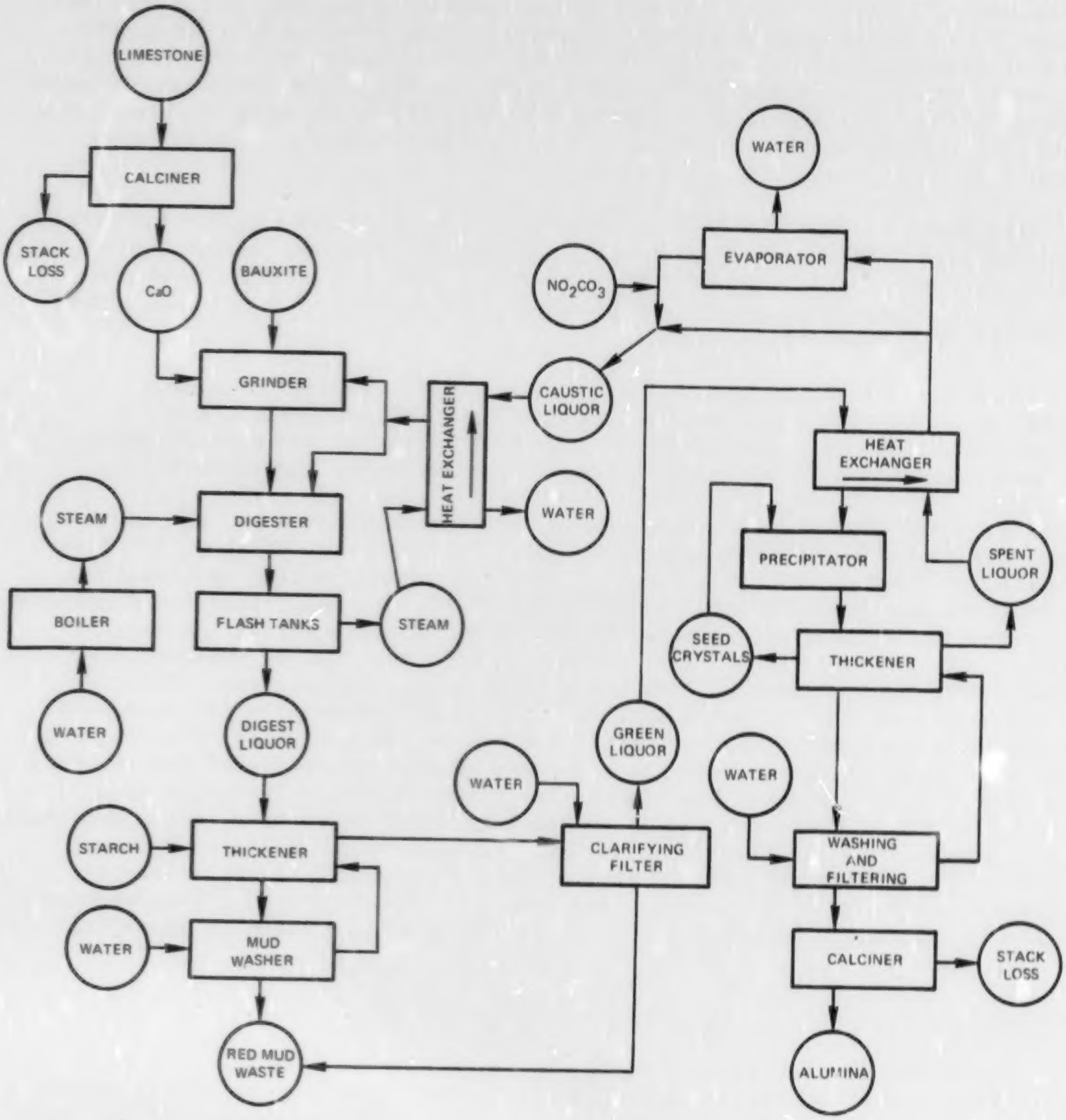

LIMESTONE
CALCINER
STACK LOSS
CaO
BAUXITE
GRINDER
HEAT EXCHANGER
CAUSTIC LIQUOR
WATER
EVAPORATOR
NO2CO3
STEAM
DIGESTER
WATER
BOILER
FLASH TANKS
STEAM
WATER
DIGEST LIQUOR
STARCH
THICKENER
WATER
MUD WASHER
RED MUD WASTE
WATER
CLARIFYING FILTER
GREEN LIQUOR
HEAT EXCHANGER
PRECIPITATOR
SPENT LIQUOR
SEED CRYSTALS
THICKENER
WATER
WASHING AND FILTERING
CALCINER
STACK LOSS
ALUMINA

Figure B-1. Bayer Process for Producing Alumina

(2) Removal of Impurities

After the digestion step, the insoluble components of the bauxite, primarily the oxides of iron, silica, and titanium, are removed by thickening and filtration. The separated solids, known as red mud, are discarded. Silica is a paritcularly undesirable impurity in bauxite, especially in the form of clay, since it is readily dissolved in the caustic liquor. Although silica is rapidly rejected from solution as a complex sodium aluminum silicate ($3Na_2O.3Al_2O_3.5SiO_2.5H_2O$), these sodium aluminum silicates cause problems with equipment scaling and filtration and the precipitate carries with it proportionate amounts of alumina and sodium.

The Bayer process can be modified, i.e., the so-called combination process which permits a treatment of high-silica bauxites. However, in the United States this process is used only on high-silica domestic ores which produce alumina that largely goes into the production of refractories and uses other than that to produce aluminum metal.

However, any silica present in the bauxites is rejected as sodium aluminum silicates which carry out sodium in the red mud. Also, a small amount of uncombined caustic soda is lost to the red mud in spite of water washing the red mud filter cake on the filters prior to final disposal.

Following digestion, which requires approximately one hour, the caustic slurry is cooled to its atmospheric pressure boiling point of about 250°F in a series of flash tanks. The steam flashed off during cooling is used to preheat the new fresh bauxite-caustic mixture prior to entry into the digesters. The digestion temperature is obtained either by steam-jacketing the reaction units or, more commonly, by direct injection of steam. After cooling, the residue (red mud) is removed from the caustic slurry in thickeners followed by filtration of the red mud underflow. Ten to 20 pounds of starch are used as a flocculating agent to help settle the red mud in the thickeners. Dilution with warm water or spent liquor is also used to aid separation of the red mud from the pregnant liquor. The red mud discharged from the thickener goes to a mud washer filter where the mud is washed with water to recover sodium hydroxide which goes back to the thickener and into the main pregnant liquor process stream. The quantity of red mud removed from the caustic slurry following digestion varies with the bauxite used and can range from 0.33-2 tons per ton of alumina produced. About 0.8 ton of red mud per ton of alumina is typical in U.S. plants.

(3) Precipitation

The resulting main process stream sodium aluminate solution goes to a clarifying filter and the clarified "green liquor" then goes to precipitation. This liquor, now clarified and diluted, is cooled in a heat exchanger to 120°-140°F and placed into large precipitation vessels that are seeded with alumina trihydrate crystals and mildly agitated to precipitate dissolved alumina trihydrate, according to the following reaction:

$$2NaAlO_2 + 4H_2O \rightarrow Al_2O_3.3H_2O + 2NaOH.$$

Approximately 50% of the alumina is precipitated during a 34-36 hour period in the precipitation vessels. The resulting trihydrate is separated by settling and filtration. A portion of this precipitate is stored and used to seed subsequent green liquor. The product trihydrate is finally washed to minimize caustic soda losses during the filtration step. Spent liquor goes on to a spent liquor treatment operation and the product (washed alumina hydrate) goes to calcination.

(4) Spent Liquor Treatment

Spent liquor is a caustic solution containing about half of the sodium aluminate originally present before precipitation. This is recycled to the process for reuse. The uncombined caustic content of this solution will be low as a result of dilution during settling and filtration, and losses of soda as complex sodium aluminum silicates removed in the red mud. However, this spent liquor represents a large inventory of sodium aluminate that is still present in the solution. The free caustic content of this recycle liquor is increased by a combination of evaporation of excess water and the addition of makeup caustic to increase the caustic concentration to the desired level of digestion.

Caustic makeup may be accomplished by adding caustic soda directly, but more typically it is produced in the process by addition of lime and soda ash according to the following reaction:

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3$$

The latter method is presently preferred and is used almost exclusively now in the United States because the alumina plants have found it difficult to obtain caustic soda and because lime is required in any case to causticize the sodium carbonate formed in the process. Typically, a portion of the spent liquor is taken off at this point and evaporated to higher concentrations to precipitate sulfates which tend to build up in the system with time. Sulfates may also be controlled by contact of the spent liquor with red mud during the clarification step by use of spent liquor for dilution.

The consumption of chemicals is also a function of the composition of the bauxite. Most of the caustic soda is recycled but makeup is required to replace losses and the amount consumed by the silica as sodium aluminum silicate. The loss of caustic is approximately equivalent to 90% of the silica content of the bauxite. Typical makeup requirements per ton of aluminum produced are 100-200 pounds of soda ash and about the same amount of calcined lime. Lime used in the Bayer process is usually obtained from selected high-grade limestone calcined at the quarry or at the Bayer plants. It requires about 1.8 tons of limestone to produce a ton of lime.

The range of soda ash and lime requirements (lb per ton of alumina) are as follows:

Soda ash	100-200 lb
Lime	100-200 lb.

Limestone requirements to produce the above amount of lime are 180-360 lb of limestone per ton of alumina.

(5) Calcination

In most U.S. Bayer alumina plants, the resulting alumina hydrate is calcined to rotary kilns which operate at about 2100 °F to remove moisture and water of hydration. The resulting alumina is so-called pot feed alumina, which is the raw material for the production of aluminum metal via the Hall-Heroult electrolytic reduction process.

(6) Raw Materials Consumption

Bayer plant operations vary since bauxite used from the several Caribbean sources differs in composition and causes variations in the consumption of raw materials, chemicals, and thermal energy. The bauxite required to produce a ton of alumina via the Bayer process depends upon the alumina content of the bauxite, the amount of trihydrate and monohydrate present, and the impurities, such as silica, iron, and titanium.

(7) Power Consumption

The power consumption in the Bayer plants is mainly for grinding the bauxite, with lesser quantities used for grinding lime and for driving mixers, rotary kilns, pumps, etc. The power consumption for grinding is a function of the hardness of the bauxite. Power consumption per ton of alumina has been variously estimated at 160-300 kWh/ton of alumina. These estimates have been made on the assumption of trihydrate bauxite feed to the plant, and on the basis that it is previously crushed. With monohydrate bauxite, power consumption for grinding is as much as 40% greater. The above range of estimates of power consumption per ton of aluminum is based upon a crushed bauxite. It does not include any power costs for crushing. Actually, about one-quarter of the bauxite imported into the United States is in the form of crude, undried, uncrushed bauxite. If one takes this into account and the fact that these imports contain up to 15-20% monohydrate, we believe that the average power consumption per ton of aluminum is more nearly 275 kWh/ton of aluminum than the consumption estimated previously by others.

(8) Fuel Consumption

Fuel is used in the refining stage mainly to generate steam for digestion and evaporation and also for firing the calcining kilns. Steam consumption has been estimated to vary as follows:

Trihydrate-based bauxite plants - 3000-8000 lb steam/ton alumina, and

Monohydrate-based bauxite plants - 4500-14,000 lb steam/ton alumina.

Most of the major alumina producers have their own limestone quarries because a high grade of lime, and thus limestone, is required to avoid introduction of impurities into the system. The lime calcination is carried out at the quarry or at the aluminum plant and therefore is an energy requirement of the process.

Since limestone requirements range from 0.09-0.18 ton per ton of alumina and the heat requirements for calcination are 4.25 x 10^6 Btu per 1.8 tons of limestone, the thermal energy requirements for lime calcination range from 0.21-0.43 x 10^6 Btu per ton of alumina.

There is also a thermal energy requirement for the calcination of alumina which has been variously estimated to range from 2.7-5.0 x 10^6 Btu per ton of alumina, depending on the size and efficiency of the calcination system. We believe that the average fuel requirement for calcination in the U.S. Bayer plants is about 4.0 x 10^6 Btu per ton of alumina.

Table B-1 summarizes the ranges of materials and energy requirements in U.S. alumina plants and the considered averages.

TABLE B-1

BAYER ALUMINA PRODUCTION
RANGE OF REQUIREMENTS AND CONSIDERED AVERAGE REQUIREMENTS
Present U.S. Operations - Conventional Technology

	Range	Considered U.S. Industry Average
Raw Materials:	ton/ton Alumina	ton/ton Alumina
Bauxite		2.40
Limestone	.09 - .18	.133
Soda ash	.05 - .1	.075
Starch	.005- .01	.006
Power:	kWh/ton Alumina	kWh/ton Alumina
	200 - 300	275
Fuel:	10^6 Btu/ton Alumina	10^6 Btu/ton Alumina
Steam generation	4.4 - 11.3	7.33
Lime calcination	.21 - .43	.31
Alumina calcination	2.8 - 5.0	4.00
TOTAL		11.64

b. Hall-Heroult Reduction Process

There are 31 U.S. aluminum reduction plants producing primary aluminum from refined alumina. All of these use the conventional Hall-Heroult process.

(1) Electrolytic Reduction

This is an electrolytic reduction process in which alumina is continuously dissolved in molten cryolite in the cell wherein aluminum is liberated at the cathode and oxygen at the anode. The oxygen liberated at the anode reacts with the carbon anode to produce CO_2 and CO. The overall reaction for the reduction of alumina by the Hall-Heroult process is as follows:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

The anode gas will also contain some CO as the result of back reaction of aluminum dissolved in the electrolyte reacting with CO_2 as follows:

$$3CO_2 + 2Al \rightarrow Al_2O_3 + 3CO$$

The anode gas is typically 50% by volume CO_2 and 50% CO.

The basis of this process is that alumina (Al_2O_3) dissolves readily in molten cryolite (Na_3AlF_6), forming a eutectic at 16% Al_2O_3 at 1725°F. The electrolytic reduction is conducted at 4.6 volts and at or near the temperature of the electrolyte. The cell electrolyte contains 80-85% cryolite, 5-7% calcium fluoride (CaF_2), 5-7% aluminum fluoride (AlF_3), and 2-8% alumina.

(2) Hall-Heroult Cells

Modern Hall-Heroult electrolytic cells are large steel boxes lined with insulating refractory and carbon. Carbon blocks at the bottom of the cell serve as the cathode in the electric circuit. During electrolytic reduction, aluminum metal in molten form is deposited as liquid at the bottom of the cell on the surface of the carbon cathode. This pool of molten aluminum is the active cathode resting upon the carbon cathode blocks at the bottom of the cell which form a connector to steel conductor support members which eventually connect to the cathode bus. Cathodes are more or less a permanent installation. Typically, the cathodes last three to six years, about the same as the life of the cell itself, after which time the cell is taken out of service, rebuilt, and refitted. Cathodes are purchased from carbon producers, while anodes are produced at the aluminum plants.

(3) Anode Systems

The anodes are also carbon suspended in the electroylte from above on steel connector rods that connect to the anode bus. The carbon anodes used in the reduction cells are produced by two methods, Soderberg or prebake. In both systems a combination of petroleum pitch and petroleum coke is used to produce the anodes. In the Soderberg system, so-called Soderberg paste is fed continuously into the top of the steel Soderberg casing in which the heat from the cell and current flow bakes the paste and removes the volatiles. In the prebake system, the volatiles are removed by making the anodes in a separate anode-forming prebaking operation.

The prebake system has a number of advantages over the Soderberg system. It requires significantly less energy than the Soderberg system and, because the anodes are baked in separate facilities, it is easier to recover the volatiles released from the anode paste.

In the Soderberg system where the prebaking of the anodes is occurring above the cell, it is complicated and difficult to recover the volatile hydrocarbons in the presence of fluorine and fluorides, CO_2 and CO, by a simple collection system. Also, power consumption is higher in Soderberg systems because expensive electrical energy is used to bake the paste. For these reasons, it appears that the prebake system will be used in new facilities and may eventually be substituted for Soderberg systems in existing plants.

Of the two anode systems used, the prebake system is the older of the two, but in the past the Soderberg system had two main advantages:

- Capital costs were lower for small smelters, because the Soderberg system avoided the cost of separate anode-making and -baking facilities; and

- It was easier to produce large cross sectional block anodes that were required in large cells.

By way of further explanation, the Soderberg system uses an anode which is baked by the reaction heat from the cell itself and resistance heat generated by the current passing through the paste. The carbon paste is used as the anode material and is fed to the top of the anode casing. As the paste moves down, it is baked, forms the anode, and then is consumed as carbon doxide is formed and released. The carbon that is removed is replaced by the paste injected into the top of the anode and thus becomes a continuous anode-making process.

(4) Production of Prebaked Anodes

In the prebake system, prebaked anodes are manufactured in a separate installation from high-purity petroleum coke, which is ground, calcined, and blended with pitch to produce a paste which can be pressed into high-density shapes. Approximately 1975 pounds of petroleum coke plus about 444 pounds of pitch are required to produce a ton of anode carbon. The coke is either purchased calcined or is calcined at the plant and ground, and is mixed with pitch in a ratio of about 4 pounds of ground, calcined coke to 1 pound of pitch. This is mixed and pressed into shapes of the required anodes. The pressed anode blocks are then baked at temperatures up to 2000°F for periods as long as 30 days (baking and cooling period) and fitted with steel connector rods which support the anode and provide a connection to the anode bus. Molten cast iron is poured into the anode socket to make a good electrical connection between the steel rod and the carbon anode. As mentioned above, these anodes are consumed by oxidation of the carbon and are replaced as required to prevent the steel from contaminating the cell electrolyte and the aluminum.

(5) Cell Operation

Aluminum reduction cells operate continuously with periodic additions of alumina and electrolyte additives, replacement of anodes, and removal of molten aluminum. Aluminum is removed periodically at one- to three-day intervals and blended with the output of other cells to attain a uniform purity level. The blended material is degassed and cast into ingots or sows or is delivered as molten metal to fabricating plants.

In addition to aluminum additions, there are periodic additions of fluorspar, namely, calcium fluoride (CaF_2), aluminum fluoride (AlF_3), and cryolite (Na_3AlF_6), to make up fluorine losses. Fluorine is released at the anode from partial reduction of the electrolyte. Approximately 50 pounds of fluorine are released per ton of aluminum produced.

(6) Energy Consumption

(a) Electric Power

Energy is consumed primarily in the form of electric power, but thermal energy is also required for anode baking and casting. Modern Hall-Heroult cells, using a prebaked anode system, typically draw 150,000-160,000 amperes operating across a relatively small voltage drop, typically in the range of 4-5 volts; a 4.6-4.7 voltage range is common in the U.S. industry. The smelting step is by far the most energy-intensive in the aluminum production sequence. Power consumption per short ton of aluminum ranges broadly from a low of 12,400 to as high as 20,000 kWh/short ton of aluminum. Historically, the United States has had the advantage of relatively low power costs, so that power consumption has been moderately high, in the range of 14,000 to 18,000 kWh/short ton of aluminum. The average is currently about 15,600 kWh/short ton.

Power consumption in the smelting of alumina to aluminum metal is basically the result of a trade-off between power costs and capital investments required in the cell. In France and Switzerland, the power costs have been relatively high. Producers have reduced power consumption considerably - to the range of 12,400 to 13,600 kWh/short ton. On the other hand, countries with cheap power costs, such as Canada and Norway, report 15,000 to 17,250 kWh/ton. We have recently had reports that in the best cell lines power consumption can be as low as 12,000 kWh/ton in prebaked Hall-Heroult type cells. This is about the minimum attained to date in the most modern cells. It is a target that could be reached if all the cell lines were modernized by installation of large Hall-Heroult type prebaked cells using the most modern present day technology. This would require an enormous investment by industry and would be difficult to justify, unless the cost of power increases very dramatically, at which time the oldest, most inefficient plants would be modernized or closed down.

(b) Fuel

In addition to the power required in the aluminum smelters, there is also the requirement for thermal energy for calcining green coke and baking anodes and for casting sows or semifinished forms.

Most aluminum smelters today are purchasing calcined coke so the energy requirements for calcination of petroleum coke are presently being carried out at the refineries prior to shipment to the aluminum smelters. The fuel for calcination is no longer a major consideration at the smelter. With the fuel availability and waste gases and waste heat at the refinery, the calcination is more logically carried out on a larger scale at the refinery rather than on a small scale at the carbon plants of the aluminum smelters.

However, there is an energy requirement for the production of the prebaked anodes. It has been variously estimated to be in the range of 2.3 to 3.6×10^6 Btu/ton of aluminum. We believe that the average requirement in modern baking installations would amount to about 2.6×10^6 Btu/ton of aluminum. This is the net energy input to the baking, i.e., external fuel used in baking. Combustible gases and part of the tar used in the anode forming are baked out in the anode-baking operation and burned at the top of the baking ovens with air lances to control pollution emissions and provide some direct heat to the baking. The amounts lost are modest, roughly 222 lb of material per ton of anodes, but only amounting to about 100 lb of fossil fuel values per ton of aluminum. The Btu value of the material would be about 10,000 - 12,000 Btu/lb, but it would be extremely difficult in the typical layout baking operation to recover this material.

Requirements for casting range from 1.5×10^6 Btu/ton of aluminum for simple casting of the aluminum metal in the form of sows to a requirement of 11×10^6 Btu for production of semifinished forms such as a product mix of 35% rolling slabs, 35% extrusion billets, and 30% sows. We believe, however, that the average is about 4×10^6 Btu/ton of aluminum for casting. This means that the total average thermal energy requirement is 6.6×10^6 Btu/ton.

Table B-2 presents a range of materials added per ton of alumina and the considered average additions or consumptions of alumina, cryolite, aluminum fluoride, calcium fluoride, petroleum coke, and petroleum pitch. It also presents the range of power and fuel consumption and considered averages in U.S. smelters.

(7) Energy Conservation - Existing Plants

It is well recognized that the major energy-consumption in the aluminum industry is in the reduction cells. In theory, the minimum amount of energy required to produce aluminum from alumina in the cell is about 35% of that used in the present electrolytic process. There are two main reasons for the relative inefficiency in comparison to theory of present electrolytic Hall-Heroult reduction cells. These are: (1) the back reaction of aluminum at the anode with CO_2, forming alumina and CO; and (2) the resistance in the cell electrolyte and the anode and cathode hardware.

The back reaction of aluminum to alumina results from molten aluminum in the cathode pool agitated by the large current flux to the anode where it reacts with CO_2 to form CO and alumina. This back reaction reduces the Faraday efficiency of the cell interface where the back reaction occurs. Increasing the distance between the anode and cathode reduces this back reaction, but it also increases the voltage drop (resistance) across the

TABLE B-2

HALL-HEROULT ALUMINUM SMELTING RANGE OF REQUIREMENTS AND CONSIDERED AVERAGE REQUIREMENTS

Present U.S. Prebaked Plant Operation - Conventional Technology

	Range	Considered U.S. Industry Average
Raw Materials:	ton/ton of Aluminum	ton/ton of Aluminum
Alumina	1.91 - 1.95	1.93
Calcined petroleum coke	0.43 - 0.60	0.52
Pitch	0.10 - 0.20	0.15
Cryolite	0.01 - 0.05	0.035
Aluminum fluoride	0.01 - 0.05	0.02
Calcium fluoride		0.003
Power:	kWh/ton of Aluminum	kWh/ton of Aluminum
	14,000 - 18,000	15,600
Fuel:	10^6 Btu/ton of Aluminum	10^6 Btu/ton of Aluminum
Baking anodes	2.3 - 3.6	2.6
Casting	1.5 - 11.0	1.5(*)

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* Simple casting of sows.

electrolyte. A more practical measure would be to reduce the turbulence of the metal and the electrolyte interface where the back reaction occurs. Improved stability of the molten aluminum pad can be achieved by operation at the lowest possible temperature that will maintain the electrolyte in a liquid state and constant control of alumina concentration. Over the past 20 years, back reaction has been reduced by 10-20%.

It is well known that if the anode current density is reduced, the turbulence of the bath between the anode and cathode can be reduced, as a result of which the back reaction is reduced slightly. Alternatively, the anode/cathode distance can be reduced, as a result of which the voltage drop across the bath becomes lower and the power consumption per ton of aluminum is reduced. In either case, the power input to the cell is lower and therefore production rates are lower. For example, by reducing the anode current density by 20%, one can expect an increase in efficiency of about 15%. However, if production is to be maintained, more cells would have to be added. Thus more investment is necessary to reduce power consumption, and this is the trade-off that must be made in an existing operation.

Moreover, any substantial reduction in current flow or voltage drop to the cell will produce a drop in the heat generated in the cell. To continue to maintain the necessary high operating temperatures, typically 1650°F, in the cell, after such improvements, heat losses would have to be reduced. This can be accomplished by increasing side and bottom insulation which, of course, requires additional capital investments.

Small energy savings can be achieved through better control of the cell operating parameters. One company reports a 3% improvement in energy through better control of the molten aluminum pad depth, the anode/cathode distance, and more frequent additions of alumina in the cell.

Quality control of anode baking should improve operating uniformity and could reduce the voltage drop in the anode. A total of all of these measures could reduce consumption in existing plants by 5-10%.

Some longer range improvements can be attained in the overall situation, since the newest smelters that have come on line in recent years have exhibited energy-consumption rates of between 6 and 7 kWh/lb of metal. This is an efficiency improvement of about 15-20% over past average smelter efficiencies due to the application of a number of measures to reduce the voltage drop, e.g., decreasing back reaction and better control of operating parameters.

Until recently, it was thought that energy conservation would be improved in the industry if existing Soderberg processes, which have tended historically to be higher in energy consumption, were replaced with prebake systems. However, one company (Japan's Sumitomo Chemical) is licensing the technology for a modified Soderberg system that involves a series of relatively small modifications that combine to provide a claimed 12-20% reduction in power consumption, a 50-100% extension of cell life, and sizable reductions in emissions of hydrocarbons and fluoride gases, plus a reduction in labor requirements. This company will discuss few details of its improvements, which include changes in operating procedures as well as equipment design but a process description is given in Chemical and Engineering News (August 4, 1975; American Chemical Society). Sumitomo claims 14,000 kWh/metric ton of aluminum, which amounts to 12,700 kWh/short ton as compared with U.S. and European Soderberg cells that operate in the range of 14,500 to 16,300 kWh/short ton of aluminum. The company claims that this results from a series of improvements, such as improved cell stability minimizing voltage fluctuations.

Typical drops across the Soderberg cells are 4.7-5 volts, depending on the alumina content of the electrolyte. When the alumina content of the electrolyte falls below 1%, the voltage can rise rapidly, as much as 30 volts;

at 100,000-165,000 amperes, small changes in voltage drop mean major changes in power consumption per ton of aluminum produced. For example, an average reduction of 1 volt out of 5 volts is a 20% effect and would have a 20% effect on power consumption.

The means of controlling voltage fluctuations are: (1) control of alumina content of the electrolyte to proper levels by more frequent alumina additions, and (2) altering the heat balance to the cathode by matching a given cathode material with a proper insulation configuration to optimize temperature differences throughout the cathode. Control of voltage fluctuations can have the following effects: (1) prolonging the working life of the cathode blocks from a previous average of 3-4 years before lining failure and shutdown,* and (2) reducing operating maintenance labor from about 1.4 to about 0.65 man-hours per short ton.

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*The average life of modified cells in one company's plants is now about 6 years, which is double the previous life, and has been as high as 8 years.

APPENDIX C

CURRENT POLLUTION PROBLEMS AND EFFECTIVENESS OF AVAILABLE POLLUTION CONTROL TECHNOLOGY

1. WATER POLLUTION

Water pollution regulatory constraints imposed upon the bauxite refining and primary aluminum smelting segments of the aluminum industry are mainly the result of Sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended. The Act provides for the Environmental Protection Agency to issue effluent limitations guidelines applicable to the point source discharge of industrial wastewater. For specific industry categories, the effluent limitation guidelines are based on technical studies commonly referred to as the "EPA Development Documents." The function of the Development Document is to characterize the industry, describe the sources of water pollution, the wastewater characteristics, control technology currently in use, suggested permissible effluent levels, recommended technology for their attainment, and cost estimates for the implementation of such technology. For this study, general information on the sources of wastewater, wastewater characteristics, treatment technology, and treatment cost estimates has been extracted from the Development Documents pertaining to the bauxite refining* and primary aluminum smelting** segments of the aluminum industry.

a. Bauxite Refining

(1) Present Sources of Wastewater

The principal waste streams in the refining of bauxite using the Bayer process are:

- Red-mud stream,
- Spent liquor,

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*"Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Bauxite Refining Subcategory of the Aluminum Segment of the Nonferrous Metals Manufacturing Point Source Category," U.S. Environmental Protection Agency, EPA 440/1-73/019, October, 1973.

**"Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Primary Aluminum Smelting Subcategory of the Aluminum Segment of the Nonferrous Metals Manufacturing Point Source Category," U.S. Environmental Protection Agency, EPA/440/1-73/019a, October, 1973.

- Condensates,
- Barometric condenser cooling water,
- Miscellaneous cooling-water streams,
- Miscellaneous waste streams, and
- Storm water run-off.

Each is briefly described below:

Red-Mud Stream

Red-mud is the insoluble residue remaining after extraction of the alumina from bauxite. After filtration or thickening to separate the pregnant sodium aluminate liquor from the red-mud gangue, the mud is pumped to disposal. If not already at a pumpable consistency, it is first diluted. Depending on the specific bauxite ore used, the residue may range between 0.33 to 2.0 tons per ton of aluminum produced. The red-mud is typically disposed in a large red-mud lake where the solids settle and the transport water is recycled.

Spent Liquor

To ensure proper process control, it is necessary to purge soluble contaminants that build up in the aluminum hydroxide precipitation circuit. This is sometimes done by evaporation and results in a salt slurry that must be disposed of.

Condensates

The bauxite refining process uses a large amount of steam in the numerous heating and evaporation steps. Most of the steam is generally condensed and reused for various plant operations, i.e., boiler feedwater and product washing. In some plants where the water balance is excess, some condensates may be rejected as a wastewater stream.

Barometric Condenser Cooling Water

Barometric condensers are widely used in the bauxite refining industry and are large consumers of water. In plants with an excess water balance a certain portion of barometric condenser cooling water is rejected as a wastewater stream.

Miscellaneous Cooling Water Streams

In bauxite refining there is typically a certain amount of non-contact cooling water used for air compressors and other cooling duties.

Storm Water Run-off

Bauxite refinery sites occupy large areas. Depending on local climatic conditions, storm water run-off can comprise a significant fraction of the total wastewater stream. Typically, storm water run-off is collected, but during heavy rainfall events excess stormwater must be diverted and discharged.

2. Waste Characteristics

Red-Mud

Red-mud consists of a solid fraction composed of insoluble particles and a soluble fraction. Table C-1 shows a representation composition of these two fractions:

TABLE C-1

REPRESENTATIVE COMPOSITION OF RED-MUD**

Insoluble Fraction		Soluble Fraction	
SiO_2	5.5%	Al_2O_3	2.5g/kg liquid
Al_2O_3	12.0%	NaOH	3.7g/kg
Fe_2O_3	49.5%	Na_2CO_3	1.6g/kg
P_2O_5	2.0%	Na_2SO_4	0.4g/kg
CaO	8.0%	NaCl	0.7g/kg
Na_2O	3.5%	$Na_2C_2O_4$	0.1g/kg
TiO_2	5.0%	pH	12.5
MnO_2	1.0%	BOD	6 ppm
Miscellaneous (including $CO_3{}^=$)	1.5%	COD	148 ppm
Loss on Ignition	11.0%		

Spent Liquor

Salts from the salting-out evaporator purge step consist mostly of alkaline Na_2SO_4.

Condensates and Cooling Water Streams

These streams may be slightly contaminated with alkaline dusts.

3. Effluent Limitations

In effect there is a single effluent limitation applicable to the bauxite refining segment.* This limitation covers all three effluent treatment levels, i.e.:

a. Best Practicable Control Technology Currently Available (to be implemented by 1977),

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*Federal Register, April 8, 1975 and April 10, 1975.

**Source: EPA Development Document.

b. Best Available Technology Economically Achievable (to be implemented by 1983), and

c. Standards of Performance for New Sources (applicable to plants constructed prior to 1983),

and reads as follows:

> "(a) Subject to the provisions of paragraph (b) of this section, the following limitations establish the quantity or quality of pollutant properties which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available: There shall be no discharge of process wastewater pollutants to navigable waters.
>
> (b) During any calendar month where may be discharged from the overflow of a process wastewater impoundment either a volume of process wastewater equal to the difference between the precipitation for that month that falls within the impoundment and evaporation within the impoundment for that month, or, if greater, a volume of process wastewater equal to the difference between the mean precipitation for that month that falls within the impoundment and the mean evaporation for that month as established by the National Climatic Center, National Oceanic and Atmospheric Administration, for the area in which such impoundment is located (or as otherwise determined if no monthly data have been established by the National Climatic Center)."

As delineated above, the regulatory requirements applicable to the bauxite refining segment are essentially a qualified zero-discharge requirement.

4. Treatment Technology

A major segment of the industry already operates its wastewater system in essentially a zero-discharge mode. Table C-2 summarizes the steps that must be taken (and are being taken by many plants) to achieve the qualified zero-discharge requirement.

5. Disposal Cost

The costs of achieving the zero-discharge requirement are largely the cost of red-mud pond construction, piping, neutralization, and any other equipment necessary for the proper operation of a recycle system. Table C-3 summarizes disposal cost data for a number of representative plants. The costs range from $0.27 to $0.60/short ton of alumina.

6. Wastewater Treatment Energy Consumption

Practically all of the energy required for the impoundment of red-mud and other waste streams is merely the electrical energy associated with pumping the waste to the pond and returning treated water to the process.

TABLE C-2

SUMMARY OF EFFLUENT REDUCTIONS ACHIEVED FOR BAUXITE REFINERY PROCESS WASTES USING BEST PRACTICABLE TECHNOLOGY CURRENTLY AVAILABLE

Waste Stream	Parameters	Best Practicable Control Technology Currently Available	Effluent Reduction Achievement
Red Mud	TDS, TSS, alkalinity	Impound & recycles aqueous phase; concentrate if necessary	No discharge
Spent cleaning acid	TDS, sulfates, pH	Impound in red mud lake	No discharge
Salt slurry from salting out evaporator	TDS, sulfates, alkalinity	Impound in red mud lake or landfill	No discharge
Barometric condenser cooling water	TDS, heat, alkalinity	Cool and recycle	No discharge
Barometric condenser C.T. blowdown	TDS	Impound in red mud lake	No discharge
"Hose-down" and cleanup streams	TSS, TDS, alkalinity	Recycle to process	No discharge

Source: EPA Development Document

TABLE C-3

SUMMARY OF WASTE DISPOSAL COST DATA

Item	Plant							
	A	C	D		E [(c)]	F		B
			Old Pond[(b)]	New Pond[(b)]		Old Pond[(d)]	New Pond	
Plant Capacity, ton/yr	904,000	358,000	832,000	832,000	1,433,000	617,000	617,000	1,268,000
Bauxite Type	Surinam	Arkansas	Arkansas	Arkansas	Jamaican	Surinam	Surinam	Jamaican
Mud Ratio[(e)]	0.33	2.0	2.0	2.0	1.0	0.33	0.33	1.0
Lake Capacity, tons dry mud	4.63×10^6	12.2×10^6	8.3×10^6	12.9×10^6	59.0×10^6	3.3×10^6	1.9×10^6	-
Capital cost, $	1.51×10^6	1.21×10^6	0.93×10^6	2.77×10^6	12.8×10^6	1.69×10^6	1.10×10^6	-
Unit Capital cost, $/ton mud	0.318	0.1	0.11	0.22	0.22	0.635	0.59	0.54
Annual cost, $/yr	355,000	102,000	502,000	-	768,000	223,000	-	-
Mud, ton/yr	226,000	728,000	1,675,000	-	1,279,000	206,000	-	-
Unit Annual Costs,								
$/ton mud	1.57	0.14	0.29	-	0.60	1.09	-	0.43
$/ton alumina	0.53	0.27	0.58	-	0.60	0.36	-	-

Notes:
(a) Mud basis, in 1975 dollars (ENR Construction Cost Index - 2126).
(b) Construction costs of old pond were expended as incurred; new pond on capitalized basis.
(c) Exemplary plant, zero discharge of pollutants.
(d) Annual costs represent average costs for two old ponds.
(e) lb mud/lb of alumina produced.
(f) Very large lake; estimated capacity includes 20-year life still remaining.

1 ton = 2000 lb   1 metric ton = 10^6 gm   454 gm = 1 lb

SOURCE: EPA Development Document

Based on a red-mud generation rate of 1.5 tons of mud/ton of alumina, and a total pumping head of 200 ft, the unit energy requirement for wastewater treatment is 7.75×10^{-4} million Btu/ton of alumina, which is a very small fraction of the total alumina production energy requirements.

Plants employing clarification devices for chemically treating (via precipitation) wastewater prior to recycle will have a small additional energy requirement.

b. Primary Aluminum Smelting

1. Present Sources of Wastewater

The potential sources of wastewater from primary aluminum smelting include:

(a) Wet scrubbers used on potline and potroom ventilation air.

(b) Wet scrubbers used on anode bake furnace flue gas.

(c) Wet scrubbers used on casthouse gases.

(d) Cooling water used in casting rectifiers and in fabrication.

(e) Boiler blowdown.

These sources are very much interrelated to the type of air pollution control systems used for particulate and fluoride control. The following overview is taken from the EPA Development Document to describe this interrelationship.

An Overview of the Interrelationship of Anode Type, Process Technology, Air Pollution Control, and Water Pollution Control*

"In the development of Effluent Limitation Guidelines for the Primary Aluminum Industry consideration was given to the interrelationship of a number of factors. The following discussion is concerned with the various ways in which primary aluminum smelters have approached environmental control. The purpose of this overview is to identify major factors.

"The specific factors that must be considered are:

Anode Type

- Prebake
- Horizontal Stud Soderberg
- Vertical Stud Soderberg

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*Source: EPA Development Document.

- Air Pollution Control Method
  - Hooding
  - Gas Cleaning
  - Dry Scrubbing
  - Wet Scrubbing
    - Once-through Water
    - Recycle Water
- Anode Bake Furnace Gas (Prebake Anode Only)
  - Wet Scrubbing
  - Electrostatic Precipitators

Anode Type

"A major factor is that no Soderberg type plants have been constructed recently, nor have any been predicted for future construction. The principal advantage of this type of cell is the absence of a requirement for an anode baking furnace.

The factors of electrode type most pertinent are those related to air pollution control and include the efficiency with which cells using the various anode types may be hooded, the nature of emissions to the air associated with each anode type, and the air pollution control devices applicable to each. It is obvious that water is not used directly in any of the types of anodes.

The major effect of differences in anode type on water usage and streams are that for prebake anode plants, cell emissions (e.g., fluorides, SOx, COx, etc.) are separate from anode bake plant emissions (e.g., tars and oils, etc.). etc.). In Soderberg type operations, all of these substances are emitted from the cell area. Current practices with regard to control (and water usage) are discussed below.

Hooding

"The efficiency of hooding of cells is a factor which determines the air pollution control measures required. In general, the results of current practice are that if (given proper operation) hoods are sufficiently tight and efficient, air pollution control devices may need to be applied only to primary pot gas to meet atmospheric emissions standards. This gas may be characterized as containing relatively high concentrations of pollutants and is suitable for treatment by either dry or wet gas cleaning devices. If hooding is of lower efficiency, emissions standards may necessitate the treatment of potroom or secondary air which may be characterized as containing relatively dilute concentrations of pollutants, and the only practicable treatment is by wet gas-cleaning devices.

Dry Scrubbing

"Dry gas-cleaning methods involve the use of dry alumina as an adsorbent to remove pollutants from the pot gas. The salient features of dry scrubbing are that the adsorbent (alumina) subsequently is fed to the cells to be reduced to aluminum metal, and that the recovery of fluoride values is virtually complete. As mentioned above, dry scrubbing is applicable only to gas streams with relatively high concentrations of pollutants, i.e., from cells with highly efficient hoods.

The total recycle of emissions has associated with it the potential problem of build-up of trace metals and impurities in the product.

Wet Scrubbing

"Wet gas-cleaning methods as practiced in the industry include wet electrostatic precipitators, tower-type scrubbers, or spray type scrubbers, alone or in combination, and with or without demisting devices. All may be classed as low pressure-drop devices, i.e., 1-10 inches of water. No high energy venturi type scrubbers are used in current practice. Wet scrubbing devices may be applied to either relatively concentrated (pot) or dilute (potroom) gases.

The scrubbing media are of paramount interest to this study and may be described in terms of recirculating type systems or once-through systems.

Anode Bake Furnace Gas Scrubbers

"In prebake anode plants, the anode bake furnace gases may be controlled by electrostatic precipitators or most commonly by wet scrubbers - again of the "low" pressure-drop types. If wet scrubbers are used, the waste waters contain tars, oils, SOx, COx, as well as fluorides if anode materials are recycled from the electrolytic cells.

Applications of electrostatic precipitators are relatively limited because of hazards stemming from arcing and subsequent burning of tars and oils in the precipitators. Gas cooling sprays generally are applied, resulting in some wastewater. Such sprays are not designed to scrub fluorides, although some incidental scrubbing action may occur, hence, the dry electrostatic precipitator is not always an adequate component to meet fluoride air emissions regulation. Baghouses are unsuited to this purpose because of the blinding action of the tars and oils. Thus, wet scrubbers are in some cases the only adequate air pollution control devices for anode bake furnaces at this time.

Current Practice

"The current practices as determined during the effluent guidelines program are indicated by the following annotated citations of existing examples illustrative of the combinations of the factors under discussion:

A. (1) Plant A. Prebake Anode - totally dry scrubbing on pot gas (zero water)

Anode Bake Plant - controlled firing

(2) Plant C. Prebake Anode - wet scrubbing on pot gas, once-through water; dry scrubbing on some pot gas

Anode Bake Plant - wet scrubbing

(3) Plant D. Prebake Anode - wet scrubbing of secondary air; scrubber water recycle with two-stage treatment before discharge

Anode Bake Plant - wet scrubbing with once-through water

B. (1) Plant B. Vertical Stud Soderberg - wet scrubbing of pot gas - total recycle of scrubber water - bleed stream evaporated - dry scrubbing planned

C. (1) Plant J. Horizontal Stud Soderberg - wet scrubbing; dry systems on paste plant

(2) Plant F. Horizontal Stud Soderberg - wet scrubbing on pot gas once-through water; dry scrubbing planned

"Some noteworthy factors in the above practices include further variations of the center-break and side-break technologies within the prebake class of plants. The center-break variation, where cell crusts are broken and alumina charged at spots along the center of the cell is potentially the most amenable to tight hooding and dry scrubbing. The side-break technology is less amenable to tight hooding and thus may lead to a choice of wet scrubbing of secondary air. Major emphasis is placed on the fact that the anode configuration in side-break cells allows higher electrical efficiency (6 kWh/lb) relative to center-break cells (7-8 kWh/lb).

"The factor leading to the planned conversion of a vertical stud Soderberg plant from wet scrubbing (but zero discharge of water) to dry scrubbing was a need to meet a stack opacity standard which was currently exceeded during pin changes.

"It also may be noted that one horizontal stud Soderberg plant has a current compliance program dependent on the installation of a dry scrubbing system."

(2) Waterborne Pollutants from Aluminum Production Employing Existing Technology

The following wastewater constituents were found to be present in wastewater emanating from primary aluminum production:

Suspended solids,

Dissolved solids,

Chemical oxygen demand (COD),

Oil and grease,

Fluoride,

Chloride,

Sulfate,

Free cyanide, and

Trace metals (including Zn, Cu, Ni).

The proposed effluent limitation guidelines set specific limitations only on:

Fluoride, and

Suspended solids.

Unlike many of the industries, there is not a great deal of available information on the raw wastewater pollutional loadings. (There is a great deal of information in the Development Document (see Table C-4) on the pollutional loadings of treated effluents, but very little on the raw wastewater).

Since wastewater flow rates and the quantities of pollutants present are so highly dependent upon the specific type of air pollution control equipment used (wet vs dry), it is not realistic to set forth a "typical" raw wasteload for the primary aluminum industry. The raw wasteload varies greatly from plant to plant.

Generally, plants utilizing a once-through treatment system will have a unit wastewater flow rate of 4,000-40,000 gal/ton of aluminum. The fluoride concentration in the untreated wastewater typically varies from 20-50 ppm. The design calculations for the Development Document treatment cost estimates assume that for a plant producing 250 ton/day of aluminum, the wastewater flow rate will be 5 million gal/day, and will have a fluoride concentration of 35 ppm.

(3) Effluent Limitations

Three levels of effluent limitations are proposed for the primary aluminum industry. These are listed below, along with the technology recommended for their attainment:

Best Practicable Control Technology Currently Available

The recommended effluent limitations for the primary aluminum smelting subcategory to be achieved by July 1, 1977, and attainable through the application of the best practicable control technology currently available are as follows:

Effluent Characteristic	Effluent Limitations(a)			
	Single-Day Maximum (b)		30-Day Average (c)	
	kg/kkg Al	lb/ton Al	kg/kkg Al	lb/ton Al
Fluoride	2	4	1	2
Suspended Solids	3	6	1.5	3

pH Range 6-9

(a) Effluent limitations are defined as kilograms of pollutant per metric ton of aluminum produced or pounds of pollutant per short ton of aluminum produced.

(b) The single-day maximum is the maximum value for any one day.

(c) The 30-day average is the maximum average of daily values for any consecutive 30 days.

The best practicable control technology currently available for the primary aluminum smelting subcategory is the treatment of wet scrubber water and other fluoride-containing effluents to precipitate the fluoride, followed by settling of the precipitate and recycling of the clarified liquor to the wet scrubbers as a means of controlling the volume of wastewater discharged. Two precipitation methods are currently available: cryolite precipitation and precipitation with lime. This technology achieves attendant reduction of the discharge of suspended solids and oil and grease.

Alternate technologies for achieving the recommended effluent limitations include dry fume scrubbing and total impoundment.

Best Available Technology Economically Achievable

The recommended effluent limitations to be achieved by July 1, 1983, by application of the best available technology economically achievable are as follows:

Effluent Characteristic	Effluent Limitations(a)			
	Single-Day Maximum (b)		30-Day Average (c)	
	kg/kkg Al	lb/ton Al	kg/kkg Al	lb/ton Al
Fluoride	0.1	0.2	0.05	0.1
Suspended Solids	0.2	0.4	0.1	0.2

pH Range 6-9

(a) Effluent limitations are defined as kilograms of pollutant per metric ton of aluminum produced or pounds of pollutant per short ton of aluminum produced.

(b) The single day maximum is the maximum value for any one day.

(c) The 30-day average is the maximum average of daily values for any consecutive 30 days.

The application of the best practicable control technology currently available results in a relatively low-volume, high-concentration bleed stream. The best available technology economically achievable is lime treatment of such a bleed stream to further reduce the discharge of fluoride. This technology also achieves further reduction of the discharge of suspended solids and oil and grease.

Alternate technologies for achieving the recommended effluent limitations include dry fume scrubbing and total impoundment.

New Source Performance Standards

The recommended standards of performance for new sources attainable by the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, are as follows:

Effluent Characteristic	Standards of Performance (a)			
	Single Day Maximum (b)		30-Day Average (c)	
	kg/kkg Al	lb/ton Al	kg/kkg Al	lb/ton Al
Fluoride	0.05	0.1	0.025	0.05
Suspended Solids	0.1	0.2	0.05	0.1

pH Range 6-9

(a) Standards of Performance are defined as kilograms of pollutant per metric ton of aluminum produced or pounds of pollutant per short ton of aluminum produced.

(b) The single day maximum is the maximum value for any one day.

(c) The 30-day average is the maximum average of daily values for any consecutive 30 days.

The best available demonstrated control technology, processes, operating methods, or other alternatives consists of dry scrubbing of potline air, the control and treatment of fluoride-containing waste streams by recycle and treatment of any necessary bleed stream by lime precipitation, and the treatment of casthouse cooling water and other streams, as required, for oil and grease removal with a gravity separator or aerated lagoon.

(4) Cost of Treatment

For the types of wastewater treatment proposed in the Development Document, most of the capital cost and a large portion of the operating cost is directly dependent on the volumetric flow rate of wastewater treated. If this varies over a wide range, the costs will also vary over a wide range.

The costs presented in the Development Document (and adjusted to 1975 dollars) are broken down by process alternative as shown in Table C-4.

TABLE C-4

COSTS OF VARIOUS ALTERNATIVES FOR FLUORIDE REMOVAL

Process Alternative	Discharge Fluoride lb/1000 lb	Capital Cost* $/annual ton	Total Operating Cost $/ton	Energy Use**		
				Electrical (kWh/ton)	Thermal, Equivalent (kWh/ton)	Total
Dry scrubbing	0	48.6	19.8	233	0	233
Wet scrubbing - once-through	5	9.0	4.5	84	200	284
Wet scrubbing - recycle	1	12.2	7.5	394	200	594
Recycle with bleed and filtrate treatment	0.05	14.0	8.4	85-395	200	285-595
Once-through and alum treatment	1	22.2	16.7	100	-	100
Once-through and activated alumina treatment	0.25	11.8	9.4	100	-	100
Once-through and hydroxylapatite treatment	0.25	26.6	24.0	100	-	100
Once-through and reverse osmosis treatment	0.8	-	29.7	100	-	100

* $/annual ton = total capital cost divided by annual production rate.

** Includes energy required by the scrubbing process in addition to that required for the wastewater treatment.

NOTES

1. Capital costs have been adjusted to 1975 dollars (ENR - 2126).
2. Operating cost includes:
    a. Depreciation @ 7.1% of capital investment
    b. Return on investment @ 20% of capital investment
    c. Admin. overhead @ 4% of operating and maintenance
    d. Taxes and insurance @ 2.0% of capital
    e. All energy and chemicals associated with the treatment plant.

2. AIR POLLUTION

a. Emission Sources

The base line for this work is aluminum produced using the Bayer-Hall process. Within the Bayer plant, bauxite is ground and digested to produce sodium aluminate. The major source of emissions during this operation is the ore grinder. After precipitation, alumina trihydrate from the Bayer plant is calcined in a rotary kiln to produce alumina. The kiln is usually equipped with a particulate collection device to recover the alumina dust for economic reasons. However, the exhaust from the primary control device may still require additional cleaning to meet standards.

At the aluminum reduction plant, alumina is reduced to aluminum in an electrolytic cell. This operation produces particulate, sulfur, and hydrocarbon emissions as well as fluoride emissions. The amount of emissions depends upon the type of cell used.

(1) Prebake Cells

The electrolytic reduction of aluminum produces a CO exhaust at the anode of the cell. As the exhaust leaves the cell, it entrains particulates including fluoride salts. The exhaust also contains noxious gases such as HF and traces of H_2S.

In a prebake plant the carbon anode, which is consumed as a part of the reaction, is formed in a baking furnace. The manufacturing process is similar to coke-making in that a paste made of pitch and coal is devolatilized forming a solid carbon anode. The process emits large amounts of hydrocarbons, sulfur compounds, and particulates.

(2) Soderberg Cells

Plants which use Soderberg cells do not require anode furnaces because the anode is formed from a coke-based paste within the electrolytic cell itself. In this case, the particulate, sulfur, and hydrocarbon emissions common to the anode furnace of a prebake cell will be emitted in the electrolytic cell of the Soderberg process instead.

There are two types of Soderberg cells: horizontal stud and vertical stud cells. With respect to air pollution control, the primary difference between these two is the ease with which a hood can be placed over a cell in order to capture emissions. In horizontal stud Soderberg cells the hood does not fit close to the pot and, therefore, large volumes of air are entrained with the hot exhaust from the cell. This has the effect of quenching combustion of hydrocarbons, thereby resulting in a large tar fouling problem as the heavy hydrocarbons condense on ducts and control equipment.

On the other hand, vertical stud Soderberg cells have close-fitting hoods so that hydrocarbon combustion can occur. In this case, the hydrocarbons are converted to CO_2 and a carbon dust which does not cause fouling.

b. Emission Rates

Typical rates of particulate and fluoride emissions are given in Table C-5. Note that fluorides can be gaseous (HF) or solid (CaF_2, NaF_2, etc.). The estimate of total particulates includes solid fluorides. As will be pointed out later, not all of the particulate control devices listed in the table are able to achieve compliance with current particulate emission standards. Plants have to rely on venturi scrubbers, electrostatic precipitators or fabric filters. SO_2 emissions are estimated to be 60 lb/ton of aluminum, but of course dependent upon the sulfur content of the pitch and coke used to manufacture the anodes (prebake cells) or anode paste (Soderberg cells).

c. Control Technology

The Bayer plant has only two sources of particulate emissions to control, as follows:

- Particulates from the ore grinder should be collected in a hood and removed using high-efficiency particulate removal, such as an electrostatic precipitator, venturi scrubber, or bag filter. Low-efficiency wet collection devices have been applied on some plants, but are generally not effective enough to comply with current standards.

- Particulates from the rotary kiln calcining operation are removed using a combination of multi-cyclone and electrostatic precipitator or bag filter. The collected dust is primarily alumina which is recycled.

The electrolytic reduction process requires controls for particulates, fluorides, SO_2, and hydrocarbons. The control technology depends upon the type of electrolytic cell being used. Table C-6 contains a summary of the pertinent emission characteristics of the three cell types. Most control systems rely primarily upon a caustic scrubber to remove particulates and gaseous hydrofluoric acid. Note, however, the following specific problems of each cell.

- Prebake cells - In addition to the control of the reduction cell, controls are also required for the anode-baking furnace. Hydrocarbon and sulfur oxides are emitted primarily in this furnace, not in the reduction cell. Incineration or flaring will be required to control the hydrocarbons. SO_2 will be controlled using SO_2 scrubbers or low-sulfur coal and pitch.

TABLE C-5
EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a]

Type of operation	Total particulate[b]		Gaseous fluorides (HF)		Particulate fluorides (F)	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Bauxite grinding[c,e]						
Uncontrolled	6.0	3.0	Neg	Neg	NA[d]	NA
Spray tower	1.8[e]	0.90	Neg	Neg	NA	NA
Floating-bed scrubber	1.7	0.85	Neg	Neg	NA	NA
Quench tower and spray screen	1.0	0.50	Neg	Neg	NA	NA
Electrostatic precipitator	0.12	0.060	Neg	Neg	NA	NA
Calcining of aluminum hydroxide[c,e]						
Uncontrolled	200.0	100.0	Neg	Neg	NA	NA
Spray tower	60.0	30.0	Neg	Neg	NA	NA
Floating-bed scrubber	56.0	28.0	Neg	Neg	NA	NA
Quench tower and spray screen	34.0	17.0	Neg	Neg	NA	NA
Electrostatic precipitator	4.0	2.0	Neg	Neg	NA	NA
Anode baking furnace[f]						
Uncontrolled	3.0 (1.0 to 5.0)[g]	1.5 (0.5 to 2.5)	0.93	0.47	Neg	Neg
Spray tower	NA	NA	0.0372	0.0186	Neg	Neg
Dry electrostatic precipitator	1.13	0.57	0.93	0.47	Neg	Neg
Self-induced spray	0.06	0.03	0.0372	0.0186	Neg	Neg
Prebaked reduction cell[h]						
Uncontrolled	81.3 (11.9 to 177.6)	40.65 (5.95 to 88.8)	24.7 (13.8 to 34.8)	12.35 (6.9 to 17.4)	20.4 (9.8 to 35.8)	10.2 (4.9 to 17.9)
Multiple cyclones	17.9	8.95	24.7	12.35	4.49	2.25
Fluid-bed dry scrubber system	2.02	1.01	0.247	0.124	0.507	0.253
Coated filter dry scrubber	1.62	0.81	1.85 to 5.93	0.93 to 2.97	0.408	0.204
Dry electrostatic precipitator	1.62 to 8.94	0.81 to 4.47	24.7	12.35	0.408 to 2.24	0.204 to 1.12
Spray tower	16.2	8.1	0.494 to 2.72	0.247 to 1.36	4.08	2.04
Floating-bed scrubber	16.2	8.1	0.494	0.247	4.08	2.04
Chamber scrubber	12.2	6.1	2.96	1.48	3.06	1.53
Vertical flow packed bed	12.2	6.1	8.4	4.2	3.06	1.53
Dry alumina adsorption	1.62	0.81	0.494	0.247	0.408	0.204
Horizontal-stud Soderberg cell[i]						
Uncontrolled	98.4 (93.6 to 104.0)	49.2 (46.8 to 52.0)	26.6 (25.2 to 28.0)	13.3 (12.6 to 14.4)	15.6 (14.4 to 16.2)	7.8 (7.2 to 8.1)
Spray tower	19.6 to 39.4	9.8 to 19.7	1.96 to 2.39	0.98 to 1.195	3.12 to 5.77	1.56 to 2.885
Floating-bed scrubber	21.6	10.8	0.532	0.266	0.343	0.1715
Wet electrostatic precipitator	7.10	3.55	26.6	13.3	1.13	0.563
Vertical-stud Soderberg cell[j]						
Uncontrolled	78.4	39.2	30.4 (20.0 to 35.0)	15.2 (10.0 to 17.5)	10.6 (5.6 to 55.2)	5.3 (2.8 to 27.7)
Spray tower	15.6	7.8	0.304	0.152	2.65	1.325
Self-induced spray	NA	NA	0.304	0.152	NA	NA
Venturi scrubber	3.14	1.57	0.304	0.152	0.424	0.212
Wet electrostatic precipitator	0.784 to 7.84	0.392 to 3.92	30.4	15.2	0.106 to 1.06	0.053 to 0.53
Multiple cyclones	3.92 to 4.7	1.96 to 2.35	30.4	15.2	5.30 to 6.36	2.65 to 3.18
Dry alumina adsorption	1.57	0.784	0.608	0.304	0.212	0.106
Materials handling[c]						
Uncontrolled	10.0	5.0	Neg	Neg	NA	NA
Spray tower	3.0	1.5	Neg	Neg	NA	NA
Floating-bed scrubber	2.8	1.4	Neg	Neg	NA	NA
Quench tower and spray screen	1.7	0.85	Neg	Neg	NA	NA
Electrostatic precipitator	0.20	0.10	Neg	Neg	NA	NA

[a] Emission factors for bauxite grinding expressed as pounds per ton (kg/MT) of bauxite processed. Factors for calcining of aluminum hydroxide expressed as pounds per ton (kg/MT) of alumina produced. All other factors in terms of tons (MT) of molten aluminum produced.

[b] Includes particulate fluorides.

[c] References 1 and 3.

[d] No information available.

[e] Controlled emission factors are based on average uncontrolled factors and on average observed collection efficiencies.

[f] References 1, 2 and 4 through 6.

[g] Numbers in parentheses are ranges of uncontrolled values observed.

[h] References 2 and 4 through 6.

[i] Reference 1.

[j] References 2 and 6.

Source: Compilation of Air Pollutant Emission Factors,
USEPA Office of Air Programs Publications.

TABLE C-6

SUMMARY OF AIR POLLUTION CHARACTERISTICS AND CONTROL

Cell Type	Particulates and Fluorides	Gaseous Fluorides	Hydrocarbons	Sulfur Oxides	Controls
Prebake Cells	Yes	Yes	Carbon dust	Trace	Caustic scrubber
- Anode Furnace	Particulates only	No	Volatiles	Yes[1]	Hot precipitator Incineration SO_2 scrubbing
Vertical Stud Soderberg Cells	Yes	Yes	Carbon Dust	Yes[1]	Caustic scrubber
Horizontal Stud Soderberg Cells	Yes	Yes	Tars	Yes[1]	Floating bed scrubber

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[1] Present in form of SO_2 or H_2S.

- Soderberg cells - Hydrocarbons and sulfur oxides are emitted in the cell along with particulates and gaseous fluorides.
  - Vertical studs - Hooding fits close enough so that hydrocarbons are burned, leaving only carbon dust. Controls include caustic scrubber or wet electrostatic precipitator.
  - Horizontal studs - The cell exhaust is diluted with too much excess air so that hydrocarbons do not burn out. Subsequent condensation of tars on ducts and control equipment creates a serious tar fouling problem. Floating bed scrubbers are often used to avoid fouling the control device with tar.

The above cell types are difficult to hood. Estimates have been made of the following coverages:

TABLE C-7

PARTICULATE EMISSION CAPTURE BY CELL HOODS

Pot Type	Amount of Particulates Captured by Best Available Hooding (%)
New prebake	95
Older prebake	79
Vertical stud Soderberg	50
Horizontal stud Soderberg	80

Because of the incomplete hooding, a large fraction of the emissions escape collection and are emitted through roof vents or monitors in the building. In some cases, roof scrubbers have been installed to remove the gaseous fluorides and some particulates. It is also possible to collect these emissions in a duct along the roof line and remove the pollutants using high-efficiency scrubbers, bag filters, or precipitators. This type of fugitive emission control is expected to be very costly but may be required to meet current standards.

3. SOLID WASTES

a. Process-Related Solid Wastes

The major source of solid wastes generated during aluminum production is the red-mud engendered during the processing of bauxite to produce alumina. This source contributes approximately 0.3 to 2 tons of solids per ton of alumina, depending on type of raw material (as shown in Table C-3).

b. Water Pollution Control - Related Solid Wastes

Most of the water pollution control systems used in the treatment of wastewater from primary aluminum smelting produce solid waste as an inherent part of their operation. However, if a wet-scrubbing system is converted to a dry-scrubbing system, it is possible to return collected particulates and gases to the electrolytic cell.

The Development Document provides limited data on reported quantities of solid waste, which are shown below:

EPA Plant Designation	Solid Waste Generation (lb/ton aluminum)
C	30
D	60
G	50-60

Calcium fluoride and inert, suspended solids are the main constituents of the solid waste.

c. Air Pollution Control-Related Solid Wastes

As noted, much of the dust generated during aluminum production from bauxite is either alumina or fluoride salts, both of which may be returned to the process.

These wastes amount to an insignificant fraction of the total solid wastes from the process - primarily red-mud.

Note, however, that the Bayer-Hall process is normally carried out in two different locations so that the dust emissions from aluminum production cannot be combined with the red-mud. In this case, the particulates are either recycled or landfilled at a cost of about $5/ton. Note that proper landfill conditions must be observed to avoid leaching fluoride salts, but there are no other hazardous constituents in the wastes requiring more extensive precautions.